Joining and Reassembling of Wood

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Abstract

Commonly the raw material round timber is reduced into smaller parts such as solid wood boards, sheets of veneer, strands, particles, and fibers for further manufacturing and processing. In following steps, the single wooden pieces are joined together by adhesive bonding to achieve the final structures such as various types of wood laminations or wood-based panels. This chapter describes the various mechanical connecting and adhesive bonding solutions. Different mechanical connector systems are introduced in theory and practice. A major part of the chapter is dedicated to wood adhesion and the basic aspects of the wood-adhesive interactions. Various adhesive types, their chemistries, morphologies, and their processes of solidification and curing are introduced, and additionally their utility in wood bonding is emphasized. Different methods of assessing and testing bond strength are also presented.

Linear-friction wood welding, as an innovative approach for bonding, which is not yet fully established in practice, is also described. Pressing processes are indispensable in the various adhesive bonding processes of wood in order to produce wood-based materials from

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veneers, particles, and fibers. Different basic pressing types and press processes are given and are discussed with respect to their application.

Keywords

Joining wood · Mechanical · Structural · Loading effects · Adhesives · Bond performance · Heat durability · Moisture durability · Adhesive-wood interaction · Pressing · Lamination · Particulate composite

14.1 Mechanical Wood Connection

Although much of the reassembly of wood materials in panels and beams are done with adhesives, the joining of larger structural components is done using mechanical connections.

14.1.1 The Need to Connect

Timber is a widely available natural resource that can be used as a valuable and sustainable construction product. Due to its natural origin, the dimensions of the solid timber are limited to those of the originating tree. The emergence of structural engineered wood products, namely glued-laminated timber (GLT) overcame these natural size limitations of structural solid timber. The only remaining limitation of individual timber members remains by the possibility to transport these members. In order to build larger timber structures and structural systems, individual structural elements are joined together by connections. It was exaggerated by McLain [1] that "a structure is an assembly of connections separated by members."

For a long time, the limitation of connection technology was one of the biggest obstacles in the development of more advanced structures. The ongoing technological progress leads to the development of new connection systems, able to carry higher loads. The role of connections, therefore, becomes crucial for the global structural behavior. Modern timber structures are able to compete with other building products such as concrete or steel.

14.1.2 Requirements for Connections

The design of the connection is crucial for the design of the entire timber structure. The design and outline of the timber structure has to be carried out in parallel to the design and outline of the connections: the size and actions in the timber member will influence the connection design and choice of the connection technology and vice versa the performance and dimensions of the connection will influence the dimensions of and demands on the timber member.

Independent of the complexity of the structure, connections have to fulfil a variety of requirements regarding, e.g., structural behavior (load-deformation behavior), reliability, durability, aesthetics, costs, feasibility, fire resistance, and many more. All these criteria are of relevance for any type of structure from small supports up to large three-dimensional truss connections. Depending on the project, the choice of the most suitable and adequate connection type might be different and require considerable effort.

The structural behavior of a connection can be described in simplified terms by the resistance, stiffness, and deformation capacity. Connections with metal dowel-type fasteners are typically characterized by an almost linear elastic behavior when being loading within the range of its serviceability limits as shown in Fig. 14.1. The collapse of the formwork for the Sandö-bridge in Sweden in the late 1930s showed that it is important to consider also the nonlinear load-deformation behavior at higher load levels reaching the ultimate limit state [2]. Considerable plastic deformation may occur within these connections. Timber shows a linear-elastic behavior until brittle failure occurs (except under compression). Hence, well-designed connections may be the only source to implement ductility in the timber structure. This can be used to create robustness and to minimize the consequences of failure of the timber structure [3]. In the ideal case, the entire load-deformation behavior of the connection is known and can be considered for the design of the timber structure [4]. At least

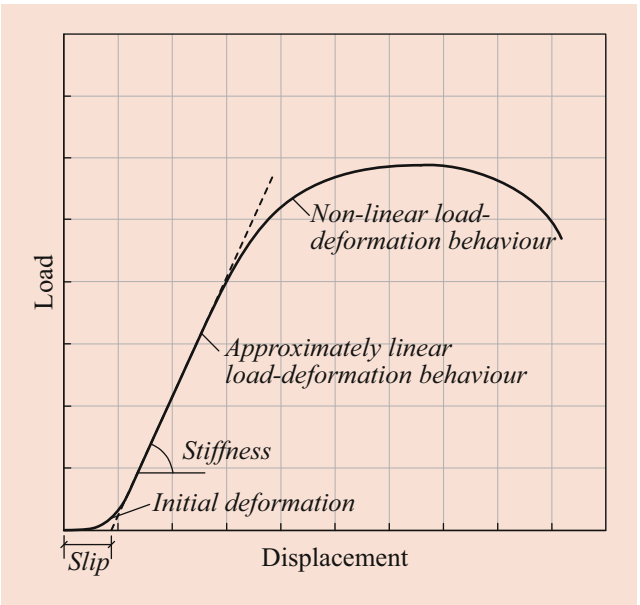

Fig. 14.1 Typical load-deformation behavior of a connection

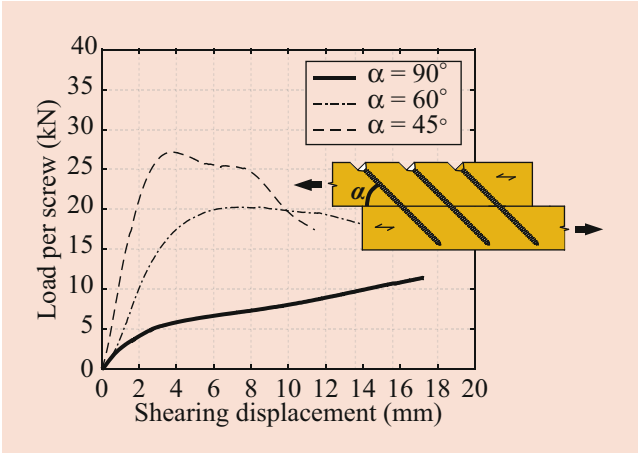

Fig. 14.2 Examples of different load-deformation behaviors for screws at different inclination. (Adapted from Ref. [5])

it should be possible to reliably predict the stiffness at serviceability limit, the load-carrying capacity at design level, and the deformation at failure.

With regard to the serviceability (usability), the stiffness of the connection is most important. Commonly a high stiffness under serviceability loads is desired. Glued connections show the best behavior with this respect [6].

The load-deformation behavior of connections can show considerable differences (Fig. 14.2) and can be described in the dependency of a variety of different characteristic parameters of both the timber and the fasteners, such as geometry; type and material; load to grain configuration; distances, spacing, concentration, and number of fasteners and size of the resulting connection; duration of loading; ambient and climatic conditions; or type of loading (one-time or repeatedly, unidirectional or alternating).

14.1.3 Typologies of Connections

The typology of the connection might be distinguished with regard to the load-carrying mechanism of the connections, which could be either by transmission of forces via contact of the timber members or transmission of forces via fastening elements. Examples of different principles of connection typologies are given in Fig. 14.3.

Challenging is especially the transmission of tensile forces in the connection since compression forces can easily be handled by contact of the members. The transmission of tensile forces requires the use of additional fastening elements. Bonding of timber by means of adhesives has been established as a technology of comparable relevance as welding of steel. The correct outline, preparation, and behavior of the adhesive bondline require special effort, treatment, and care.

In recent years, welding technologies for timber, i.e., the connection of wood members under heat and pressure by conversion of the wood cell structure, have been researched and developed (see also Sect. 14.3 of this book).

14.1.4 Developments of Connections Over Time

Since connections are among the most challenging key elements of timber structures, the connection technology reported represents the current state of the art in construction and design possibilities.

One of the oldest techniques to connect timber members is by notching or wedging or creating holes in the members to create contact connections [8]. These so-called carpentry connections transfer the forces mainly by contact of the different members (Fig. 14.4). The transfer of tensile forces requires special effort, and examples of extraordinary craftsmanship can be found, e.g., in the variety of Japanese craft connections but also old European craftsmanship, e.g., by Grubenmann in the eighteenth century [9]. The reductions in cross section reduce the strength of the members but also create stress singularities sometimes with considerable stresses perpendicular to the grain diminishing the load-carrying capacity significantly [10]. That is why carpentry connections mostly did not efficiently make use of the timber resource but allowed a variety of shear, compression, and even tension connections. Historically, wood dowels were used mainly for fixation of members, less for load-carrying purposes.

The limitation of carpentry connections with regard to the efficient transfer of high forces offers potential for applications where either the structural demand is lower or where larger areas for the transfer of forces are available. Modern examples are, e.g., CNC machined joints with multiple steps of macro [12] or micro size [13], or dovetail connections as secondary beam connections [14]. The extrapolation of traditional carpentry connections used in small sizes for furniture production (Fig. 14.5a) offers potential for modern applications with large dimensional CLT panels [15] (Fig. 14.5b). Criteria for the design of modern carpentry connections relate not only to the possible force transfer and load-carrying mechanisms (see also Fig. 14.5a) but also to the ease of production and assembly, especially in case of large dimensional CLT panels, and to the visual appearance.

In the beginning of the twentieth century, the knowledge in design of timber structures increased but was limited to the concepts of linear elastic strength theory. Research was limited to strength and stiffness of timber members. These stress-based design concepts allowed only for efficient design of connections where all parts behave linear elastically. As a result, shear connections (split ring, bulldog, etc.) were widespread at that time and major research was performed [17].

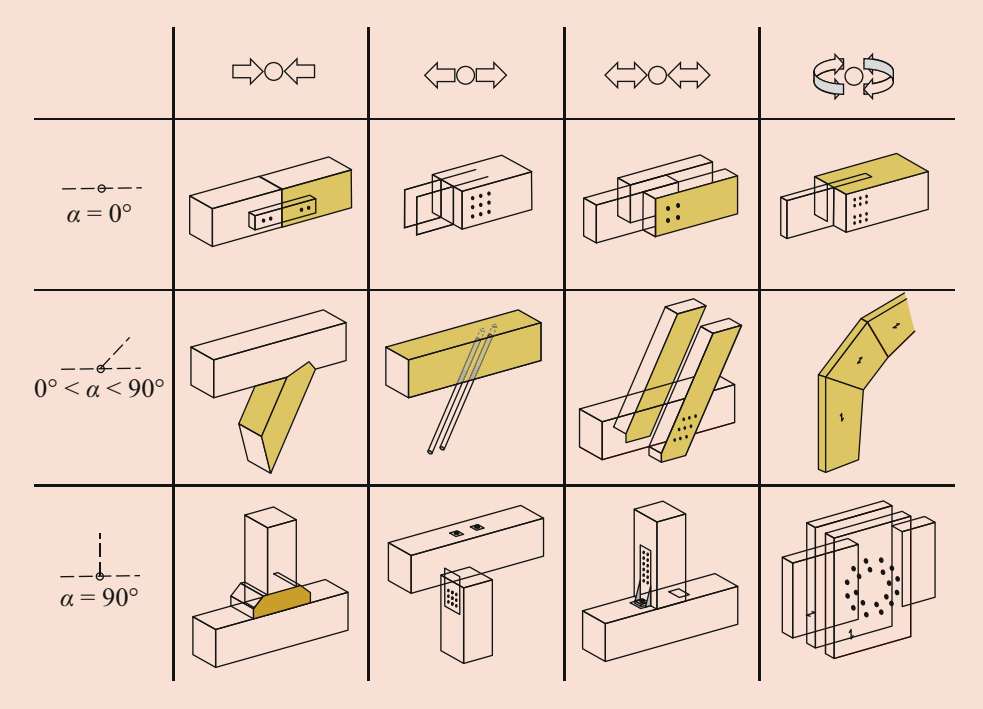

Fig. 14.3 Principles of connection typologies between timber members (ochre and brown) and steel members (gray) for different loading conditions. [7]

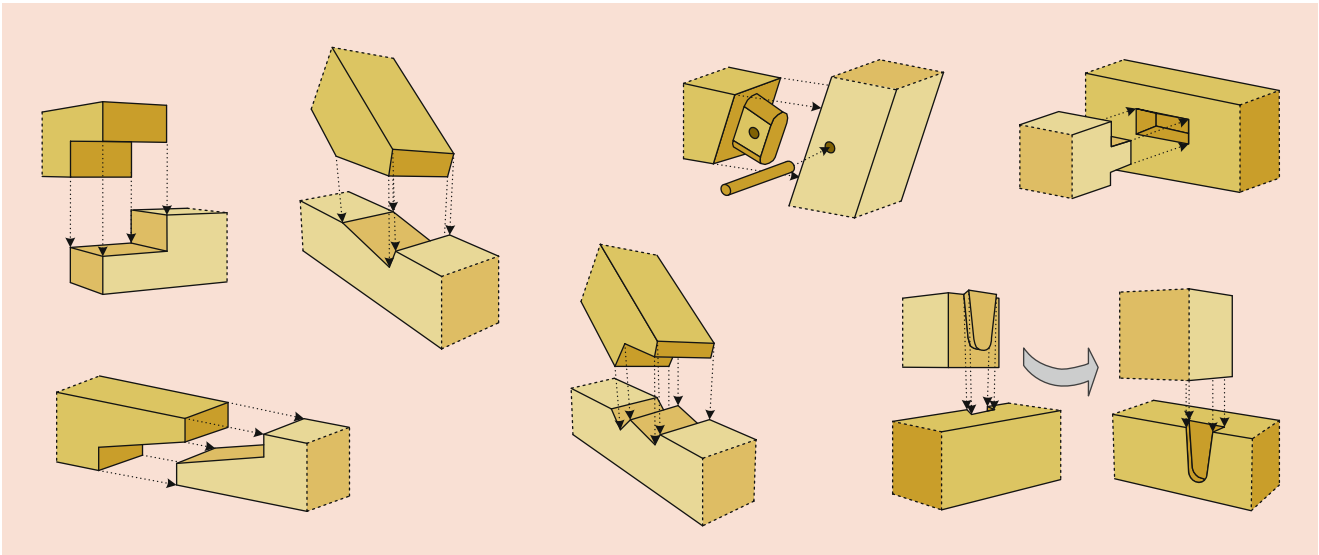

Fig. 14.4 Typical carpentry connections, which transfer the forces mainly by contact of the different members. [11]

These compact connections transfer the forces between members by embedment of the connectors in the timber. The load-carrying mechanism of these connectors is illustrated in (Fig. 14.6). The embedment (compression) stresses in the contact zone between connector and timber are further transferred through shear into the timber member. Thereby, the connectors activate only the surface layers of the timber members by shear and compression (embedment) stresses.

Dowel-type fasteners are characterized by a long cylindrical shaft, potentially a tip, and a head. Since the beginning of the twentieth century, metal dowel-type fasteners gained popularity due to their good performance and easy applicability. These fasteners offered new possibilities for the construction of large timber structures. However, the knowledge of the load-carrying behavior of nails, bolts, and other dowel-type fasteners was limited at that time, and design concepts

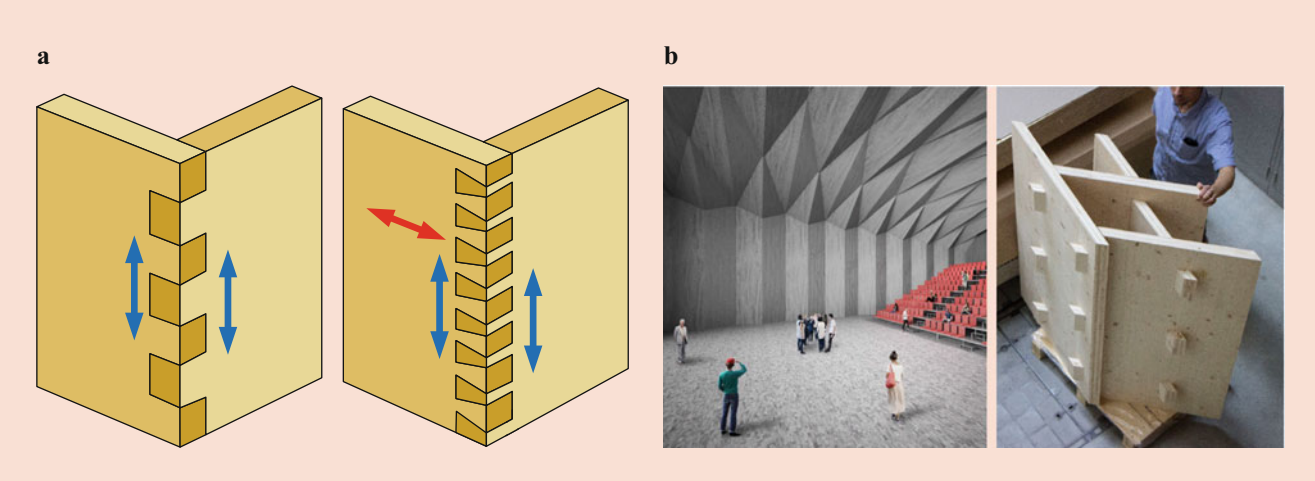

Fig. 14.5 Carpentry connections in (**a**) traditional applications for furniture and in (**b**) modern applications in large dimensional CLT elements [16]

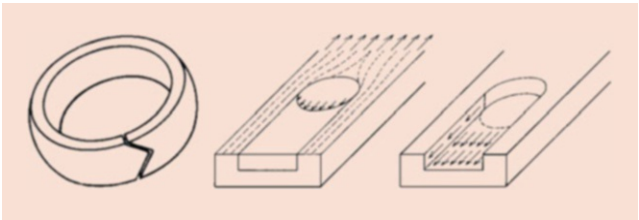

Fig. 14.6 Typical split ring connection and schematic load-carrying behavior

for nails were either based on empirical observations for certain geometries or were restricted to loading situations with pure elastic embedment [18, 19]. Prescriptive design rules based on empirical data were used at that time. Efficient design procedures for nails and other dowel-type fasteners with variable geometry and inserted in timber members of variable thickness remained to be developed.

With the adoption of plastic design theories in the timber sector in the middle of the twentieth century, it was possible to predict the load-carrying capacity of dowel-type fasteners with different geometry and slenderness in an efficient way (Fig. 14.7) [20, 21]. With the new design procedures, all different types of dowel-type fasteners could be designed in dependency of their geometry and the material properties of the fasteners and the timber [22].

In the last decades of the twentieth century, fracture mechanical design concepts have been established in the timber engineering community [23, 24]. These concepts allowed for a description of the stress states and failure mechanisms of connections in which stress singularities and fracture processes are present [25]. This is typically the case for bonded-in steel rods (though the design should not aim for these failure modes) or in glued connections in general [26]. Especially in larger adhered connections such as bonded lap joints or adhered fiber-reinforced products, the stress singularity has to be accounted for in design. Adhesively bonded connections come closest to the aim of an ideal load transfer between members with full activation of the cross-sections of the timber members [27]. Glued-in rods offered also for the first time the possibility to directly transfer tensile forces between members without creating lap joints or shear connections [28]. The challenges in production control and achievement of the correct failure mode limited the big success of bonded-in rod connections in the past.

Traditionally, screws for timber construction were produced by cutting the thread into the wire material. Thread geometries are specified, e.g., in DIN 7998 [29]. With the adoption of new technologies, such as the forging and rolling of the thread from the wire material, into the production processes of screws for timber construction at the end of the twentieth century, it was possible to manufacture new types of screws from high strength steel with diverse thread geometry and of greater thread length [30]. These new generations of screws can be produced with special screw tips which allows for an installation without predrilling of the timber. The easy installation, high load-carrying capacity, and optimization with regard to different performance criteria make these fasteners suitable for a wide range of applications. Similar to glued-in rods, self-tapping screws allow for a direct transfer of tensile forces between members [31]. Due to the anchorage of the thread in the timber leading to a high withdrawal resistance, high axial forces can be transferred [32].

In line with the development of more advanced design procedures and fastener production technologies at the present day, the development of computer controlled machining, such as CNC milling, allows to get back to the very

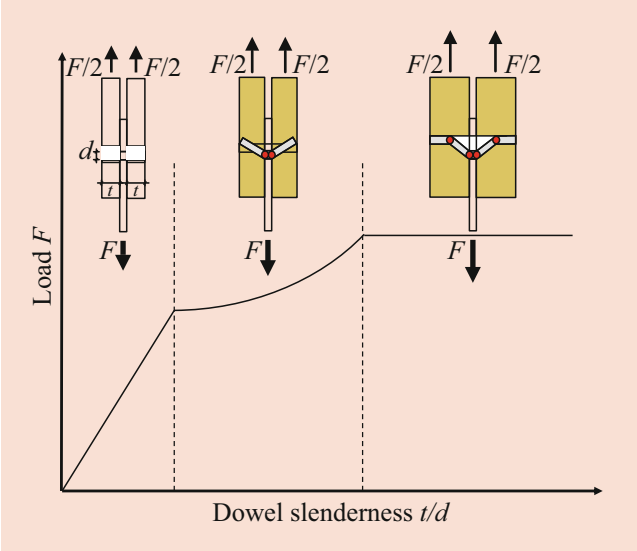

Fig. 14.7 Schematic load-carrying behavior of dowel-type connections as a function of the slenderness of the dowel-type fasteners

beginning of the development of connection technology and to apply advanced carpentry connections with high precision in an automated production of prefabricated elements.

14.1.5 Selecting a Type of Connection

Evaluations of failure events have shown that connections are involved in a considerable number of cases of failures or collapses of structures [33–36]. Hence, connections are key elements of structures enabling the transfer of loads between individual members and components. Ductility is an important issue when designing timber structures to exhibit robustness or when energy dissipation is a key need, as, e.g., in the case of strong seismic actions on structures [37].

Considering only the load-carrying capacity of a connection when designing a structure is straightforward only with statically determinate structures. In case of statically indeterminate structures, the deformation capacity of the connection is of high importance. Hence, the concept of performance-based design would be more appropriate in these cases. Performance (in terms of load-carrying and deformation capacity) based design has so far been applied mostly in seismic design of structures [38, 39], but it offers a great potential also in other design situations where the load-deformation behavior of connections is of key impact [40, 41]. Hence, better knowledge about the stiffness properties and the load-deformation behavior of connections is absolutely crucial for a more efficient and reliable design of connections in structural systems [42, 43].

One major challenge when designing connections is to reach a high degree of utilization of the timber cross-section, which can be achieved by applying high-performance connections [31, 44, 45], as, e.g., steel dowels, self-tapping screws, or glued-in rods.

Carpentry Connections

Despite their relatively low performance, the simplicity of carpentry connections with the direct load transfer by contact makes these connections being efficient even today for special situations, such as CNC machined dovetail connections. The deformation behavior is influenced by the precision of manufacturing, the load to grain angle under loading, and possible shrinkage due to variation in moisture content. For holding the elements in place and for fixation, e.g., against uplift in step joints, additional metal fasteners such as bolts or screws are used.

Shear Connections

The load-carrying capacity of shear connectors is directly related to the contact area with the timber. The stiffness of these connections can be very high if well executed. However, since the load is introduced only into the surface layers of the timber members mainly through shear and compression (embedment), an efficient load transfer between different members is hardly possible.

Bolted and Dowelled Connections

The connections most commonly applied in timber structures, besides adhesive-bonded connections, consist of metallic fasteners. Slender rod-shaped fasteners, such as nails, staples, bolts, dowels, and screws, are of highest importance for timber connections. The structural behavior of the connection is influenced, among others, by the diameter and slenderness of the fasteners, as well as the anchorage of the fasteners in the timber, i.e., the ability to transfer load not only in the lateral but also in the axial direction. The need for predrilling depends, among other factors, on the size of the fastener, the timber material (density and species), and the shape of the fasteners. Dowels are mainly loaded in shear and bending, and transfer the load by lateral pressure, i.e., embedment of the fastener in the timber. Bolts together with nuts and washers allow for an activation of the axial capacity of the fasteners (Fig. 14.8a).

Steel dowels are very cost efficient and easy to install. Especially in combination with slotted in steel plates, steel-dowelled connections are effective and allow for transferring high loads. New types of self-drilling dowels allow for an easy installation, even on site. Studies assessing the performance of dowelled connections and recommendations for further optimization of such connections can be found, e.g., in Refs. [46, 47]. The aspect of ductility with this type of

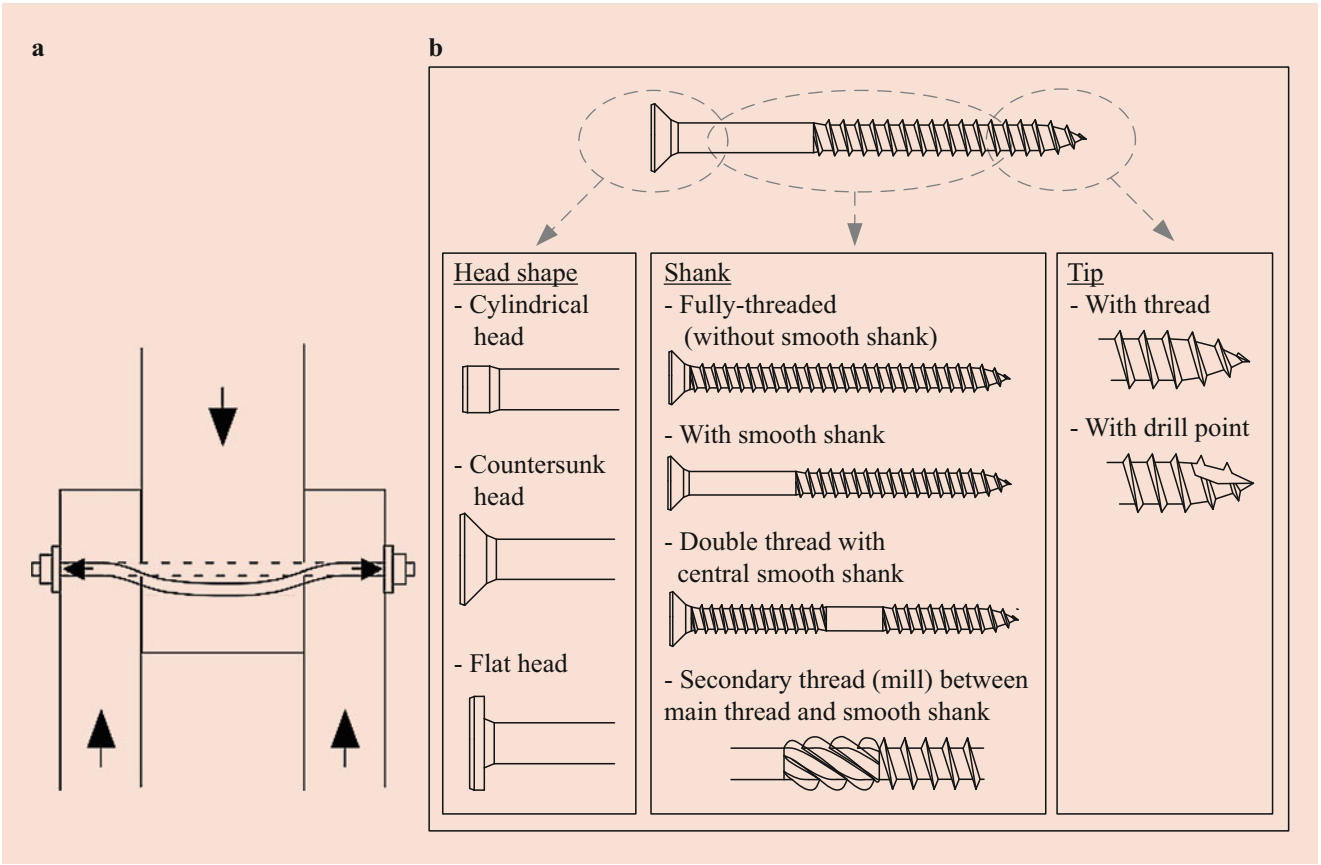

Fig. 14.8 Timber connections: (**a**) bolted connection with activation of the axial capacity of the fasteners, and (**b**) overview of different characteristics of modern, self-tapping screws

connection is constant topic of discussion in timber engineering research [4, 48, 49].

In order to achieve a high efficiency of the connection, a larger number of small diameter fasteners should be preferred against a small number of large diameter fasteners: the volume activated by the small diameter fasteners is balanced with the spacing and distances needed to avoid splitting and cracking of the connection. Dowel-type fasteners acting in multiple shear can equally load the timber members, activating the full cross-section of the respective layer and show high load-carrying capacity and stiffness. Another advantage of multiple slotted-in steel plates with fastener in multiple shear is that the steel plates are protected by the timber in the fire situation [50] and have generally a good aesthetical appearance.

Nails

Nails are among the oldest types of fasteners [51]. The understanding of the different failure modes with different plastic deformation of the nail allowed to an economic use of nails in structures [21]. The development of a variety of different shank geometries, e.g., with smooth shank, threaded shank, or annular rink shank, and the use of high steel strength makes nails being modern types of fasteners. The application of these different types of nails varies, since nails with smooth shank are not considered to carry substantial axial loads whereas threaded or rink shank nails may be loaded to a considerable amount by axial forces [52] and allow for an increase of lateral load-carrying capacity due to a rope effect [53]. Nails can be used to connect two or more timber or wood-based members or to mount steel plates and sheet metal parts onto timber elements. The relatively small diameter of nails and their long penetration length in the base material allows commonly for the development of failure modes with plastic hinges in the fasteners. The nail stuffing in magazines allows for an automated installation by means of nail guns.

Axially Loaded Fasteners and Glued Connections

One of the biggest challenges in timber engineering, the transfer of tensile forces between individual members, can be tackled by means of axially loaded fasteners, such as

screws, threaded rods or glued-in rods, or other adhesive bond connections. The transfer between the fastener and the timber can be either by mechanical anchorage of the threaded part of the rod or screw in the timber or by adhesive bonding of the bondline with the surrounding timber. The mechanical anchorage of the thread of screws in the timber allows for a very reliable load transfer whereas the adhesive bond of glued-in rods is very demanding and may be compromised by delaminations or debonding due to, e.g., moisture-induced stresses or stress peaks, respectively. The development in production technology allows for the production of long, fully threaded screws (see Fig. 14.8b) that enable for the full activation of the tensile capacity of the steel cross-section of the screws [54]. Also glued-in rods shall be designed in a way that the yield capacity of the steel cross section is limiting the load-carrying capacity in order to benefit from high ductility and the low variability of this failure mode. Besides rods, other elements can also be adhesively bonded into the timber, such as perforated steel plates [55]. These create a very easy and robust connection between different timber elements and even exhibit good performance under cyclic loading [56].

Screws and glued-in rods are suitable to introduce both tensile and compression forces. Slender fasteners loaded in axial compression may show the risk to buckle where the elastic embedment of the fasteners in the timber is beneficial [57]. Buckling commonly occurs close to the load introduction into the fastener as in the vicinity of the surface of the timber.

Specialized Connections

More advanced types of fasteners with specialized shape of shank or thread [58], of material with different quality and strength, together with different connection elements such as perforated steel plates, angular brackets, slotted-in plates or metal connector plates [59] enable highly specialized connections. This allows the creating of more economic and efficient connections [60].

Even conventional connections as described above can be optimized by means of reinforcement. The embedment strength of the timber can be enhanced by adhering panels made of plywood [61] or densified veneer wood [62] in the shear joint in the areas with the highest dowel penetration. In addition, these panels reinforce the timber in shear and tension perpendicular to the grain and reduce the risk of splitting and block-shear failure. Fully threaded screws can be used as internal reinforcement [46], enabling reduced spacing and distances of the fasteners and thus, allowing for connections with smaller dimensions.

14.1.6 Understanding the Behavior of Connections

The highly nonlinear load-deformation behavior of connections with dowel-type fasteners sets a challenge to the prediction of the correct behavior. After introducing the plasticity theory into timber engineering by Johansen in the 1940 [20], more sophisticated models for describing the entire load-deformation behavior have been developed [63–66]. Nevertheless, none of these models has established in design standards. For numerical modeling of dowel-type connections, the balance should be kept between the desired degree of detail and a reliable estimation of properties [67, 68]. Special challenges are the multiaxial stress state [69] and the complex material behavior of the wood [70, 71]. Simplified models using beam on elastic foundation or spring models can serve as a good approximation [72, 73].

Timber as a natural material exhibits considerable variability in its material properties. The material properties with highest relevance to the structural performance of shear connections with dowel-type fasteners are the embedment strength of the timber and the yield strength of the fasteners. Extensive studies on the determination of the embedment strength properties were performed in the 1980s and served as a basis for the material property values currently given in EN 1995-1-1 [74, 75]. Recent studies focused on determining respective embedment strength properties for hardwood [76]. The distribution characteristics being relevant for the reliability analysis of connections with dowel-type fasteners were evaluated by Whale and Smith [77]. A strong correlation between embedment strength and timber density was found. An extensive database with material property values has been collected within WG3 of COST Action FP 1402 [78].

Fastener yield strength depends on the steel grade used, but it shows a much smaller variation compared to the timber properties [48, 79]. Nevertheless, the determination of yield strength has been matter of discussion [80], and the so-called overstrength of the specified steel grades, i.e., the possibility of higher actual steel strength compared to the declared strength, has been appointed to be accounted for [49] especially when intending to design connections with ductile failure behavior. Although ductility has been reported as being a key prerequisite for robust timber structures [37], little guidance and support are provided to the designer, such as design rules and recommendations in design codes. This may be due to a lack of knowledge on how to assess and assign ductility ratios to connections and structures based on the choice of their material and geometrical shaping.

A first discussion of the impact of varying material properties on the structural behavior of connections with dowel-

type fasteners was published by Werner [81]. Further studies on the reliability of connections with dowel-type fasteners and on the effect of the number of fasteners in a connection (group effect) were performed by Kohler [82]. Brittle failure modes were found to be relevant especially for double shear connections with thin timber side members and they need to be accounted for in the estimation of load-carrying capacity of structures [83], although in general the design should aim at achieving a ductile failure mechanism.

14.1.7 Design of a Connection

Timber is strongest when being loaded along its fiber direction. Forces perpendicular to the grain can cause cracks (tension or shear) or large deformations (compression). In the connection, the direct loading path between two or more timber members is disturbed. Depending on the connection type, the load has to be transferred from one timber member to the fasteners and from the fastener to the other timber member. With every transfer from one element to the other, there is the risk that forces are acting at an angle to the grain direction reducing the capabilities of the connections.

These force deviations reduce the efficiency and performance of the connection. Despite the deviation of forces due to eccentricity of the different members, internal stresses due to the penetration of the fasteners and the weakening of the timber member can create splitting forces.

When designing connections, it should be generally aimed at crossing the axes of the different members in one single point in order to avoid eccentricities inducing additional forces perpendicular to the grain (Fig. 14.9a). Within the axis of the member, eccentricities can be avoided by splitting the forces into several overlapping systems, e.g., multiple slotted-in steel plates or multiple glued-in rods (Fig. 14.9b). By portioning the forces in the connections into these several subsystems, a more efficient load transfer in each connection becomes possible and more efficient connections can be achieved.

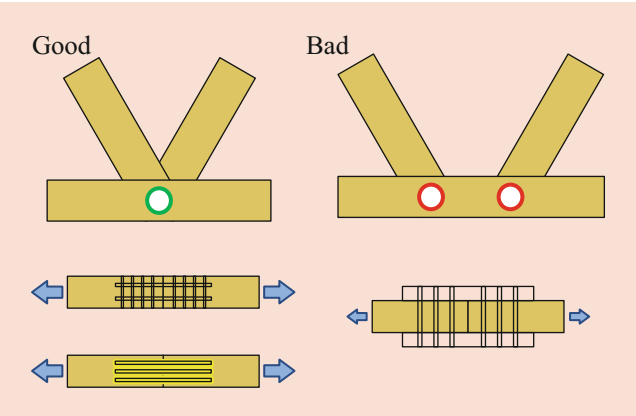

Fig. 14.9 Design principles for connections: Members should be connected so that member axes meet in one point, the deviation of forces in connections from the member axis should be minimized by using multiple, internal shear planes (such as slotted-in steel plates) or multiple tensile connectors (such as bonded-in rods)

The shape and outline of the connection is influenced not only by the performance of the single fastener but also the interaction of groups of fasteners and the corresponding edge and end distances.

The interaction of different fasteners, such as the accumulation of stresses of multiple fasteners in a row, may considerably reduce the load-carrying and deformation capacity of the connection.

Structural Behavior of Carpentry Connections

The structural behavior of traditional carpentry connections is matter of long ongoing studies [84–87]. Numerical models are commonly used to study the stresses in the contact area [88]. The significance of these studies has to be critically assessed with regard to the stress concentrations together with the brittle failure behavior of the timber, the variability of the material properties, and the possibility of shrinkage cracks in the cross sections especially of solid timber members. Research in recent years focuses mainly on the assessment and repair of existing connections [89, 90].

Structural Behavior of Laterally Loaded Fasteners

The load-carrying capacity of connections with dowel-type fasteners in timber is commonly determined as the minimum of the load-carrying capacities estimated according to the so-called European Yield Model (EYM), which is based on studies by Johansen [20]. The failure modes addressed in this model involve the embedment failure of the timber and/or the ductile failure of the dowels in dependency on the thickness of the timber members. Commonly it is aimed at a failure mode with ductile failure of the dowels, which requires a certain minimal thickness of the timber members and minimal end and edge distances of the fasteners. If these requirements cannot be fulfilled, embedment failure in the timber may occur. Simplifications of the design equations of the EYM have been discussed but never established [91–93]. More precise adaptions of the EYM account also for the friction and the actual bending angle of the fastener [53].

Additional failure modes in the timber surrounding the connection may occur, that are often characterized by brittle failure mechanisms due to excessive shear and/or tensile stresses perpendicular to the grain [94]. Neglecting the mentioned brittle failure mechanisms in the design may lead to an overestimation of the reliability of structures, especially when consisting of elements of a high timber grade [95]. Major research on the evaluation of brittle failure modes of

connections with multiple fasteners has been performed [96–99]. Geometrical parameters affecting the (brittle) failure behavior of connections include end-grain distance, spacing between fasteners, edge distances, thickness of timber members, and penetration depth of the fasteners.

Structural Behavior of Axially Loaded Fasteners

Self-tapping screws can be used in a large variety of applications for the connection between different timber members or for the connection between timber and steel parts. Screws reach highest load-carrying capacity when being loaded in direction of the screw axis [32]. That is why screws are often applied with an inclination in shear connections in order to benefit from a large contribution of their axial load-carrying capacity. Depending on the ratio of axial and lateral loading of the screw, the deformation capacity changes considerably: axially loaded screws show only a small deformation capacity whereas laterally loaded screws perform very ductile [2].

14.1.8 Further Developments of Connections

The requirements for connections are in general to be reliable, easy to install, capable of carrying high loads with high stiffness and high ductility. In certain applications, such as residential buildings, additional requirements may apply, such as acoustic isolation, aesthetics, or harmlessness to health. The urge for connections with higher performance with regard to strength, stiffness, and deformation capacity requires greater sophisticated design rules in order to allow for more economic and reliable designs and to increase the competitiveness of timber structures against concrete and steel. Timber failure modes due to unbalanced loads, stresses perpendicular to grain, and stress peaks in the vicinity of connections are challenges for the conception of design guidelines. Tasks for the further development of fasteners include the efficiency of the load transfer. The compatibility of the different materials (such as wood species, steel quality and alloy, adhesive and treatment) and the performance and durability in different environments has to be guaranteed.

14.2 Wood-Adhesive Bonding

There is a long history of adhesively bonding wood going back to early recorded history in Egypt [100] and most likely before recorded history [101–103]. Although most of the products until the twentieth century were mainly for interior use, such as furniture and cabinetry, now many bonded wood products are used for exterior applications and even building structures. During the intervening years, bonded wood products and wood adhesive technology have changed considerably with the advent of new composite and structural products, along with many types of fossil fuel-based adhesives, in addition to the expectation of greater durability [104]. The need for wood adhesives during this time involved two driving forces: (1) obtaining products that cannot be made out of solid wood (e.g., large panel products and long beams) and (2) more efficient utilization of the wood supply (e.g., particleboard) [104]. These high performance panel and beam products would not have been possible without the synthetic adhesives, and these trends are continuing with new wood products like cross-laminated timber and mass plywood panels that allow tall wooden buildings and windows that are not just inserts into wood framing, but are an integral part of the overall structural design. Thus, in addition to the traditional drivers of improved durability, better strength, and low overall adhesive costs [105], new drivers include the structural bonding of wood to other materials, such as glass, concrete, metal, fiber-reinforced polymer, and other composites.

The wood products industry has also driven adhesive development to provide improved performance including higher strength, moisture and heat durability, production processing efficiency, and lower cost [106]. While much of the development had been evolutionary up until the mid-twentieth century, at that time there was a dramatic shift to synthetic adhesives made from petroleum and natural gas instead of proteins. This change led to products that were easier to manufacture, higher in performance, and lower in cost. Although there is a lot of interest in environmentally driven factors for replacement of synthetic materials, synthetic adhesives will probably dominate for the foreseeable future with bio-based and bio-based-synthetic adhesives increasing their very small market share and especially for niche markets.

The chemistry and some application aspects of many wood adhesives are covered in ▶ Chap. 24 of this handbook (binder resins) and the literature [106–108]. Thus, our emphasis in this chapter is on a general discussion of the adhesives from their source through the chemistry to their utility, and the impact that wood and adhesive have on final product performance. Sections on individual adhesives are a summary of their chemistry with more emphasis on why one adhesive is preferred over another for certain applications, as well as the diversity of the adhesive technology.

Importantly, adhesives are not final products but are essential in holding the substrates together in the bonded products under all normal use conditions. To accomplish this role, the adhesive needs to have both strong adhesion to the wood (or other substrates), as well as cohesion within the adhesive. Adhesive chemists and users need to understand many factors because the chemistry and physical properties dominate bond formation, while the adhesive performance is generally determined by the bonded adhesive's mechanical properties

under various conditions [109]. The durability of the entire bond is very important since many bonded wood products need to continue to function for decades, and in some cases for centuries.

Adhesion is important aspect of adhesive performance and is a vital aspect for all adhesives. Adhesion has been covered in various books for non-wood substrates [110–114] and has been reviewed for wood substrates [115–117]. For many substrates, adhesion can be the main cause of bond failure, especially when bonding low surface energy plastics, including Teflon™. The debate over what provides good wood bonds has been around for many years [117–120]. The common list of adhesion theories includes the following [110, 117]:

1. Adhesive adsorption (thermodynamic and kinetic) or wetting theory covers both the gross spreading of the adhesive over the substrate, as well as the flow into the irregularities of the substrate surface, which are orders of magnitude larger for wood compared with most other substrates. This is vital to all adhesion because no bonding can take place if there are not molecular level contacts of the adhesive with the substrate surface. This spreading also covers the formation of bonds formed by van der Waals forces, including the London dispersive forces. A fresh wood surface is easier to wet than a surface where extractives are allowed to build up a rather hydrophobic wood surface [121], but other effects, such as oxidation of wood surfaces, have been less studied
2. Acid-base and other polar bond theories cover forming stronger individual bonds compared to those involving dispersive forces, and usually provide more overall interaction strength than the more numerous dispersive bonds for polar materials. The formation of polar bonds depends on the ability of functional groups on both the substrate and adhesive surfaces to have the proper orientation. Polar bonds require an electron donor on one material and an electron acceptor on the other. Polar bonds, such as hydrogen bonds, should be quite common given the large number of hydroxyl groups on the wood and various hydrogen bonding groups on the adhesives. The acid-base bond is somewhat less common but could occur between an aminoresin and the carboxylic acid groups present in wood, although this interaction has not been demonstrated. Polar bonds are often water sensitive, potentially leading to delamination under wet conditions, but this effect of water on polar bonds is likely more complicated than simple water insertion into the polar bond [122]
3. Chemical covalent bonding provides the most durable bonds, but is less likely to occur. Covalent reactions can occur on the surface, but only if the reactive groups have the right orientation and energy to react with a reactive group on the adhesive. Contrary to a common literature assumption [123], Yelle and coworkers have shown that isocyanates did not form significant covalent bonds with wood polymers under typical bonding conditions [124]; however, phenol-formaldehyde resins reacted with wood cell wall polymers [125]
4. Mechanical interlocking theory is certainly a common explanation, especially given the cellular nature of wood [119, 126–128], but it is unclear how much strength this provides, especially when the applied force is perpendicular to the bondline. A split open earlywood cell can allow adhesives to enter the lumen given its diameter of 30–40 μm for softwood tracheids and 10–20 μm for hardwood fibers, but this is not necessarily true for the larger filler particles. On the other hand, latewood cells cleaved in the middle lamella [116] are less likely to have much mechanical interlocking. Mechanical interlock does not occur without good wetting and molecular level contact of the wood by the adhesive. Although adhesive penetration of the wood lumens has been examined in two dimensions for many years by cross-sectional analysis [127], now with high-resolution tomography, the penetration can be observed in three dimensions [128]
5. Diffusion theory involves entanglement of the polymer chains of the substrate and adhesive. Although this process is common in solvent or thermal bonding of plastics, wood welding is not very common [129] (see Sect. 14.3). A more likely case for wood adhesives is for the adhesive to polymerize after infiltrating the cell wall to form an interpenetrating polymer network [130]
6. Electronic or electrostatic theory has been proposed, but it is not considered a normal adhesion mechanism. Charges or free radicals do not normally build up on wood surfaces, except after high energy irradiation, like plasma treatment
7. The theory of weak boundary layers is a bond weakening mechanism, in that some intermediate layer between the bulk substrate and bulk adhesive has low cohesive strength, leading to bond failure [131]. The wood interphase can be weak due to wood cells being fractured during surface preparation (mechanically weak boundary layer, MWBL) or resinous or oily compounds on the wood surface that serve as the weak layer (chemically weak boundary layer, CWBL) between the sound wood and the adhesive [132]. MWBL might also be caused in situ during the bonding process by the combination of high pressure, high moisture content, and high temperature, weakening the wood strength and causing fracture of the cellular structure. Weak layers in the adhesive can be caused by internal shrinkage during curing and the swelling and shrinking of wood [109, 116, 133, 134]. Extracts from the wood or flow of certain adhesive components into the wood can influence the cure at the adhesive boundary [135, 136]

Although adhesion is important, it is only part of the bond strength. Cohesive strength of the adhesive also plays a major role, especially because it serves to transfer force between the two wood surfaces. The adhesive interphase a critical zone for bond strength due to shrinkage from water loss or from curing reactions, as well as strain on the wood surface from the swelling and shrinking of the wood. Marra first pointed out the nine zones between the bulk wood on one side of the bond to the bulk wood on the other, as illustrated schematically in Fig. 14.10a [115] and with an actual bondline in Fig. 14.10b. Link 1 is the bulk adhesive is the completely formed adhesive, and failure in this zone is easy to see as cohesive failure. Links 2 and 3 are often poorly formed adhesive near the wood surface due to extractives from wood and are part of cohesive adhesive failure, but may be difficult to detect due to their thinness. Links 1 through 3 are the glueline between the wood surfaces. Links 4 and 5 is the interface between the wood and adhesive and is only a molecular layer in thickness. Links 6 and 7 is where the adhesive exist in the cell lumens and cell walls and thus alters the wood properties. Links 2–7 are the interphases as the properties change from the bulk adhesive to the bulk wood. Links 1–7 are the bondline where the adhesive is transferring the load from one wood member to another (links 8 and 9).

Most adhesive studies are done on laminates since it is the easiest way to measure both the adhesive and cohesive properties of the adhesive, as well as understand the importance of adhesive interaction with wood. This allows the researcher to detect the effect of changes in adhesive chemistry and formulation, bonding temperature and pressure, exposure to humidity and temperature, wood species, and treatment conditions, etc. However, even these studies are not always as clear as they seem due to the natural variation in the wood (earlywood vs. latewood, juvenile vs. mature wood, sapwood vs. heartwood), presence of reaction wood, orientation of wood in regards to grain angle, and tangential vs. radial planes. Thus, one is unlikely to sort out all the variables, but a lot has been learned from studying the bond performance of laminates by limiting the number of variables.

The issue becomes much more complex in studying the bonding by binder adhesives in particulate composites (strandboard, particleboard, and fiberboard) since the adhesive droplets on irregular wood surfaces are bonded under conditions where the temperature and moisture content (MC) varies with the distance from the platens, in addition to the difficult in determining where failure actually takes place. The former is also an issue with plywood, but plywood is easier to study due to the adhesive being a continuous film rather than droplets. Although some properties of the binder adhesives can be inferred by the properties of the composite board, much is also concluded by the known properties of the laminate adhesive studies.

14.2.1 Adhesive Types and Properties

Although wood adhesives have been used for a very long time with satisfactory results, detailed discussion of the adhesion mechanism did not begin to take place until McBain and Hopkins in 1925 proposed mechanical interlocking as the main factor [119]. However in 1928, Browne and Brouse argued that although mechanical interlocking was a factor,

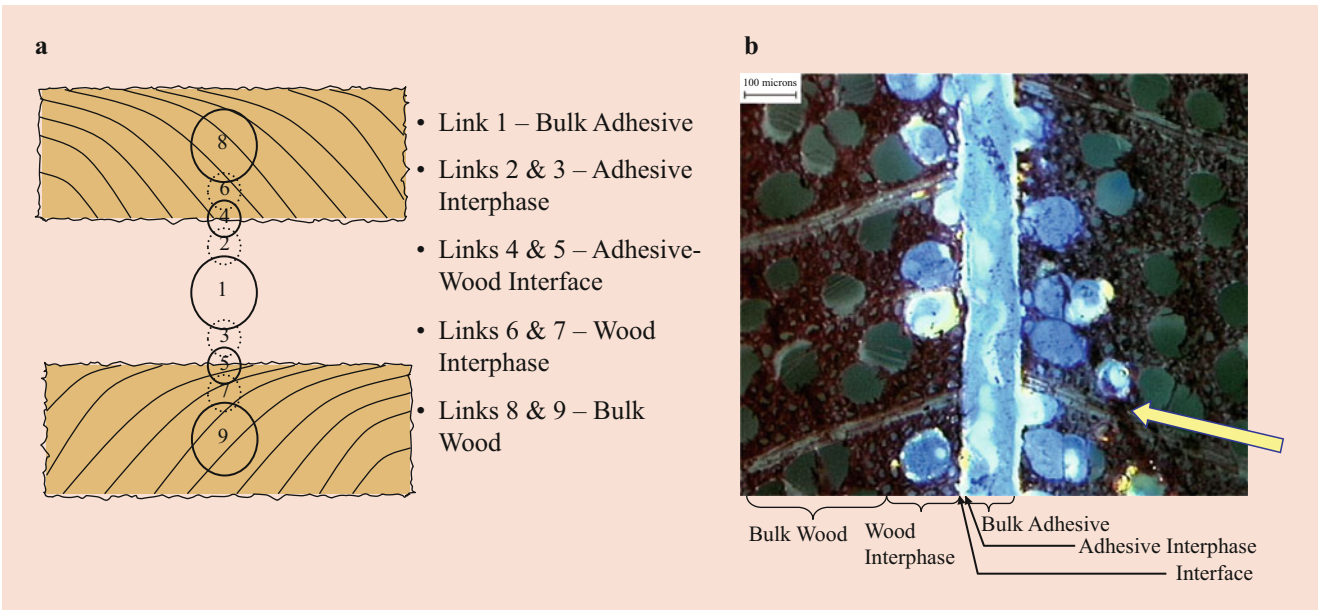

Fig. 14.10 Bondline failure zones (**a**) using Marra's illustration with links 2, 3, 6, and 7 as the likely source of failures [115] but with the terminology described in this chapter and, (**b**) an epoxy/yellow-poplar bondline cross-sectional view using fluorescence spectroscopy

even more important was the specific adhesion (adsorption) between the adhesive and the wood [118]. This specific adhesion was not well defined at that time, but certainly could include those adhesion factors listed in the previous section. As the adhesives changed from protein-based to synthetic formulations, much more has been learned about bonding wood because of the ability to greatly control the adhesive structure with regards to its morphology and molecular weight. Using these more controlled formulations, considerable information was learned about successful adhesives [107, 109, 137] and the bonding of different species of wood. Although there were some individual comparisons in the literature of different adhesives types and what factors helped or inhibited adhesion, there was no generalized model. Marra has covered many aspects of wood bonding [115, 138]. River et al. has previously pointed out the importance of the internal strain on the curing of the bond, since this strain added to the applied load during swelling and shrinking of wood causing failure under lower than expected applied loads [116, 139]. However, they did not explore the adhesive influence on this problem, especially with regards to different adhesive types.

Today, wood adhesives bond most wood species together with good dry strength and many have sufficient water resistance under light water exposure. After severe water exposure, unbonded wood expands and cups (Fig. 14.11a). This extreme wetting and drying challenges the bond so severely that even many thermoset adhesives do not withstand the testing failing within the glueline (adhesive between wood surfaces) rather than in the wood. Using knowledge gained from many individual studies, broader reviews of wood bonding, and polymer mechanics, a theory was developed that explained the relative moisture durability of different types of thermoset adhesives [140] and was also extended to include wood properties [141]. In this theory, wood adhesives belong to two general classes because of how they interact with wood and form polymer bridges between the wood pieces, what their morphology and mechanical properties are, and how they distribute interfacial strain through the wood or through the adhesive as illustrated in Fig. 14.11 to avoid bond fracture. To resist this distortion, the adhesive needs to infiltrate the wood cells near the surface to distribute the strain through the wood (Fig. 14.11b), or the adhesive needs to have some flexibility at the surface to distribute the strain through the adhesive (Fig. 14.11c). If neither of these can be accomplished, then highly cross-linked adhesives like epoxies fail near the wood surface under wet conditions [134], or a not sufficiently flexible polyurethane also fails in the adhesive interphase [142].

The largest volume of wood adhesives are the in situ polymerized class, including polyaddition or polycondensation types (Fig. 14.12) [137]. These involve adhesive monomers or oligomers (often called resins) that fully polymerize after application. The low-molecular-weight fractions of the

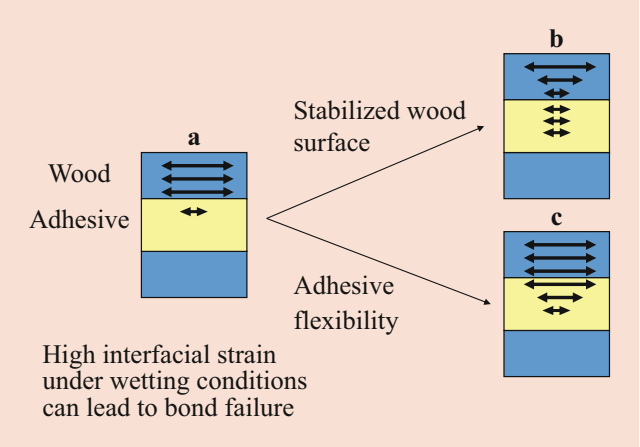

Fig. 14.11 Interfacial strain (**a**) can be dissipated by either stabilization of the wood surface by an in situ polymerized adhesive (**b**) or by the adhesive flexibility of a pre-polymerized adhesive (**c**). Arrows are for easy visualization but do not reflect the absolute amplitude of the strain [137, 139, 141]

resin allow some of them to infiltrate and cure in the cell walls to stabilize the wood surface (Fig. 14.11b). This is important since the adhesive backbone is rigid, and the polymer has a high degree of cross-linking providing it little flexibility as the wood changes dimensionally. As an example, the phenolics are extremely rigid and brittle even under wet conditions; however, they are well known to dimensionally stabilize wood towards swelling [142]. Thus, it is likely that this ability to stabilize the wood cells near the surface serves to prevent weak boundary layers in the wood or adhesive from causing premature failures. The rigid and cross-linked nature of these adhesives also prevents undesired creep (adhesive flow over time under load). Among the adhesives that fall into this class are the phenolics, aminoresins, isocyanates, and epoxies. When an in situ polymerized adhesive fails to stabilize the wood, then it most likely will have poor water resistance, as in the case of epoxies, where the epoxy fraction is unlikely to penetrate the wood [134].

The other class of adhesives are pre-polymerized adhesives, which include polyurethanes, poly(vinyl acetate)s, proteins, carbohydrates, and film, contact or hot melt adhesives [137]. As shown in Fig. 14.12, the polymeric nature of these materials makes them too large to infiltrate and stabilize the wood cell walls, although they still flow into cell lumens. The main problem with this class is that the adhesive needs enough flexibility after cross-linking to deal with the interfacial strain caused by the wood swelling, or otherwise, the adhesive interphase region becomes a weak boundary layer. They also have limited ability to repair weak boundary layers in damaged wood surface cells. However, too much flexibility allows for creep and other distortions of the bonded assembly.

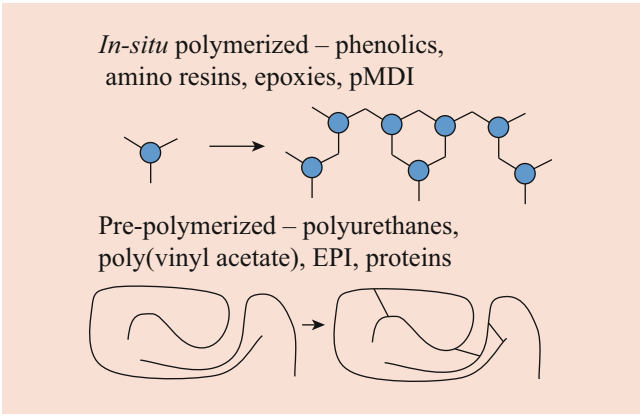

Fig. 14.12 Illustration of curing of wood adhesive classes for in situ and pre-polymerized adhesives

Independent of adhesive type, specific formulations vary according to wood species, bonding conditions, wood form (laminate, veneer, strand, particle or fiber), and expected performance of the bonded product. As an example, a plywood adhesive is high in viscosity (thousands of mPa*s) for roller type applications, while a binder adhesive for composites is low in viscosity (hundreds of mPa*s) to allow it to be sprayed.

In Situ Polymerized

The in situ polymerized adhesives, consisting of monomers and oligomers (low MW (molecular weight) polymers), need to react to form large polymers to develop sufficient cohesive strength within the adhesive [137]. The adhesive goes from liquid to solid by covalent chemical reactions and, in most cases, by loss of the water solvent. The cure can be accomplished by heat, change of pH, adding a hardener or cross-linker, or in the case of isocyanates, the presence of water. These adhesives needed considerable development of formulations prior to significant market acceptance. These synthetic adhesives raised the performance bar greatly to set today's performance criteria for bonded wood products, especially in terms of moisture resistance. A main part of this change was the movement to hot presses as the in situ polymerized amino and phenolic adhesives replaced the cold setting pre-polymerized proteins.

Amino-Type Adhesives

The aminoresins are the most widely used adhesives for wood bonding, especially for interior products, such as plywood, particleboard, fiberboard, and veneer overlays (mainly using UF resins in all products), but some are also used for water-resistant applications employing MUF resins with different proportion of melamine [106, 143, 144]. The relative low cost, colorless nature, ease of application and curing, hardness, good thermal properties, and cold water resistance

Step 1 Methylol adduct

$$R\text{-}NH_2 + H_2CO \Longrightarrow RNH\text{-}CH_2\text{-}OH$$

Where R-NH_2 is urea or melamine and H_2CO is formaldehyde

Step 2 Methylene formation

$$RNH\text{-}CH_2\text{-}OH + R\text{-}NH_2 \Longrightarrow RNH\text{-}CH_2\text{-}NHR + H_2O$$

Step 2a Bismethylene ether formation

$$2\ RNH\text{-}CH_2\text{-}OH \Longrightarrow RNH\text{-}CH_2\text{-}O\text{-}CH_2NHR + H_2O$$

Where urea has two and melamine has three R-NH_2 groups for reaction

Fig. 14.13 The two steps in aminoresin synthesis, see text for discussion of reaction conditions

are important properties of aminoresins [143, 145–147]. Although the two main aminoresins (UF, urea-formaldehyde, and MUF, melamine-urea-formaldehyde) have somewhat similar chemistries and both belong to the in situ polymerized group [140], they are different in many respects. By far the largest wood adhesive by volume is the UF type, which has been the dominant adhesive for particleboard, fiberboard, and interior plywood due to its ease of application in wood bonding, fast set, and very low cost, while the more expensive MUF co-condensate (in a few cases realized as a mixture UF + MF (melamine-formaldehyde)) can be used for exterior products [146]. MUF is preferred against pure MF for its lower cost; MF as such is not used much by itself as an adhesive, but is the resin of choice for impregnated papers used as a laminate for coated boards and laminate countertops.

Chemistry of Adhesive Formulation

Like many of the formaldehyde adhesives, the chemistry seems deceptively simple in that the amino group (urea and also melamine in the case of MUF resins) reacts with formaldehyde to attach a methylol (hydroxmethyl) group to the amine, while minimizing polymerization [144] as indicated in Fig. 14.13. Then, this intermediate reacts under altered conditions with another amino group to form a dimer by a condensation (splitting off water) with this process continuing to form oligomers and even some polymers. The first step occurs under basic or acidic conditions (depending on the molar ratio of the components) while the further condensation reaction occurs preferably under acidic conditions; thus,

these two steps can be controlled separately (for acidic conditions in the addition step, a high F/U ratio is used and provides a product with less salt content, depending on the pH used). Under these acidic conditions and heat, the condensation proceeds until the desired molecular weight (MW)/degree of condensation (DOC) is achieved (there may be some additions of urea in this stage). In order to stop the condensation reaction, the pH is raised and the temperature is lowered, and usually more urea is added in order to adjust the necessary low molar ratios before shipping the condensate, but still liquid product to the wood panel manufactures. This degree of control allows adhesive companies to adjust the type of adhesive product to production process and wood supply at individual wood product plants.

In reality, this seemingly simple process is extremely complicated, and the urea and melamine reactions with formaldehyde are different in many respects [141–143, 145]. Most of the differences have been attributed to the greater electronegativity of the melamine compared to the urea. An indication of this difference is that only three of the four sites on the two amino groups in urea react with formaldehyde under normal ratios, while all six of the sites on the three amino groups in melamine react with formaldehyde. Urea's lower reaction with formaldehyde means that the reaction works the best at high pH for the formaldehyde adduct formation. At high pH, the amino groups are better reacting with the formaldehyde. At low pH, the reaction product is protonated making it easier to be attacked by another urea in the condensation step [144–146].

Once the methylol adduct is made, lower pH condition leads to oligomerization by condensation (water loss) from these adducts. However, in addition to methylene group formation between urea molecules, there is also the formation of bismethylene ether, Fig. 14.13. This latter compound is less stable and can release formaldehyde directly to form the methylene linkages or can hydrolyze to the monomer and then release formaldehyde. Of all the formaldehyde-containing adhesives, those containing urea are easiest to hydrolyze and release formaldehyde, leading to concern about the long-term safety of formaldehyde adhesives and the UFs in particular [106, 143, 148–152]. The strength of the C-N bond between melamine and formaldehyde (now as a methylol group) inhibits hydrolysis compared to the C-N group with urea; thus resins containing melamine (depending on the proportion of melamine in the resin) can be used for exterior applications, while UFs are limited to interior applications.

Many details of the extensive studies on UF chemistry have been evaluated in the literature [106, 143–145, 153, 154] so only the key steps are discussed here. In the case of alkaline methylolation, the reaction is generally carried out by adding formaldehyde to the urea at a high molar ratio (between 2.0 and 2.2 F/U) to form urea-methylol adducts with pH greater than 8, with time and temperature being the main variables. Lowering the pH below 6 causes these adducts to be condensed to oligomers with some polymers. When the desired level of condensation is accomplished, the pH is raised to the alkaline region to slow the reaction before one or two quantities of urea are added. The manufacturer tailors the adhesive (condensation portion and free urea content, amount of linearity, and branching of the oligomer, avoiding gel particles, etc.) to the needs of the panel (plywood, particleboard (PB), and medium-density fiberboard (MDF)) or other wood products manufacturers' operations. Thus, there is no standard UF adhesive formulation, especially in Europe where the panel products can be made to various formaldehyde emission levels [106, 137, 143] depending upon the strictness authority rules and panel customer's preference.

For the MF, formaldehyde can be added to all six sites [144, 146], but the formaldehyde to melamine ratio is usually between 1.5:1 and 2:1. Besides the cost, another problem with melamine is its low solubility in water, which improves as the melamine is converted to the melamine-formaldehyde adduct, but decreases as this adduct is condensed to oligomers. To help with solubility, other organics can be added. Unlike the UF, the condensation reaction occurs at neutral as well as acidic conditions, but usually acidic conditions are used. When the proper degree of oligomerization has occurred, the pH is raised to >9.0 and excess water is removed by evaporation. The product is cooled and shipped to customers. For making MF-impregnated paper for high-pressure laminates, the MF resins needs to be low in molecular weight (MW) for good penetration into the saturating Kraft paper and high reactivity for linking the MF dispersed in the paper into a rigid product [144, 146].

Along with pH, time, temperature, and formaldehyde-to-urea (and/or melamine) ratio are important variables for aminoresins. By altering these variables during the production process, a variety of products can be made. Variations include average and distribution of MWs, linearity versus branching, ratio of methylene versus dimethylene ethers in the oligomers, and free formaldehyde in the adhesive. Some branching helps to provide a cross-linked adhesive network after curing that gives the adhesive cohesive strength, along with heat and creep resistance, but too much cross-linking can make the product overly brittle, especially for UF resins [155].

The average and distribution of MWs is a more complex situation. Low MWs allow the adhesive not only to flow well into the wood voids but also to infiltrate the cell walls. However, too low of an average MW leads to over penetration and insufficient adhesive to bridge the gap between wood surfaces (glueline). Low MWs also require more reactions to build up the adhesive network, which is commercially undesirable but these longer cure times can be

overcome mainly by lower pH conditions and somewhat by increased temperatures. Determining the ideal average MW and thus viscosity of the resin (considering the resin solid content) depends on the production process of both the resin and the wood-based panels, as well as the wood species used. Plywood and other laminations such as wood veneer overlays onto panel products are applications that require a higher viscosity adhesive to bridge the surfaces compared with the lower viscosity needed for good adhesive distribution when making particleboard and dry process fiberboard.

There are some additional compounds, which can be formed under specific conditions that can complicate the adhesive synthesis by altering the polymeric structure. For the UF, under strong acidic conditions, the trimethylol adduct can self-cyclize to give an uron structure instead of polymerization [143, 145]. For melamine formation, there are two side reactions that can form ammeline and ammelide by hydrolysis to replace amino groups with hydroxyl groups, both of which are undesirable in that their acidic nature alters the MF reactions [146].

In addition to the base polymer, the adhesive is also adjusted when needed with additives (including various flours, like rye, wheat, or wood flour) for avoiding over-penetration into the wood that lead to starved gluelines and surfactants for proper wetting of the wood surface, moisture level to prevent delamination from too wet of a bondline or moisture retention to avoid dry out of the adhesive during the open assembly time (time after the adhesive is applied and before the second wood surface is added).

The development of standards in Japan, Europe, the United States, and other countries have led to the emergence of new UF types, with low or even very low content of formaldehyde (low molar ratios of formaldehyde to urea) are labeled as ultra-low-emitting formaldehyde UF (ULEF-UF) in North America, CARB phase 2 resins, E05 in Europe, or F**** in Japan) to provide bonded products that have very low formaldehyde emissions. This has led to the development of products with even lower formaldehyde-to-urea ratios, and the addition of scavengers, such as UF resins with F/U $<$ 0.4 [143, 145]. Although ULEF-UF adhesives are capable of meeting emissions standards because UF can degrade under hot moist conditions, some wood panel manufactures are opting instead to use no-added formaldehyde (NAF) adhesives. Currently, polymethylene diphenyl diisocyanate (pMDI) is the only viable NAF adhesive for particulate panel production.

The introduction of melamine into a UF produces a MUF resin, providing an increased water resistance and a wider operating window in panel production, e.g., for better resistance against moisture variation during the process when producing PB or MDF with low formaldehyde emissions. Thickness swelling is usually also improved by using sufficient but not too high of a proportion of the high cost melamine. Several ways can be used to produce such MUF resins depending on the content of melamine, which can range from a few % (melamine-fortified UF) to >20% (MUF). The usual way to produce a MUF resin is to add both urea and melamine at the beginning of the adduction reaction (or in a certain sequence of addition) to make a random copolymer after oligomerization and adhesive curing [144, 146]. Just blending UF and MF is possible but seldom used [106, 143]. The sequence of the addition of urea and melamine determines various resin properties, such as cohesion behavior and reactivity. Another efficient way of using melamine for making good cost and good performance adhesives is to add melamine monoacetate as the curative for a UF resin, because this provides both the melamine for linking the UF chains and the acetic acid for acid curing the adhesive [144, 146], but this process does not seem to be commercially used.

In some limited cases, phenol is combined with MF/MUF resin, yielding phenol-melamine-urea-formaldehyde: PMF, PMUF with higher content of phenol and lower content of melamine, and MUPF with high content of melamine but only low content of phenol [156]. It is not fully clear if and how condensation between the aminoplastic components and the phenol occurs.

Raw-Materials Source and Cost

Aminoresins are made from urea, melamine, and formaldehyde, which are derived from natural gas and hydrocarbons that are widely available from inexpensive methane and other by-product hydrocarbons. These raw materials are first converted to syngas (carbon monoxide and hydrogen), then to methanol at a suppliers facility, and finally to formaldehyde or formalin by selective oxidation processes usually at the suppliers or adhesive producers (the latter allows production as needed reducing storage and shipping cost) [157, 158].

The urea is made from ammonia and carbon dioxide [158, 159], and is also a feedstock for making melamine by decomposing urea with amine to cyanic acid, and then cyclization [158]. In summary, the aminoresins are mainly based on nonpetroleum fossil fuel. Although UF is a very low-cost adhesive, melamine is considerably more expensive and causes the production cost of making melamine-based adhesives quite expensive relative to other wood adhesives. However, this is usually addressed by fortifying UF with melamine or making MUF resins to make more efficient use of the melamine.

With melamine-based resins of a certain content of melamine, there does not appear to be much of an opportunity to reduce raw material costs unless a new low-cost route for melamine can be developed, but formulations continue to be

optimized for making low-formaldehyde emitting versions and enhanced production rates with minimal melamine.

Adhesive formulations can also contain fillers, surfactants, waxes, or other additives to improve performance properties depending upon the application. One formulation issue that has not found a practical solution is a method to stabilize the components that lead to no formaldehyde emissions in the cured UF adhesives.

Chemistry of Cure with Conditions and Interaction with Wood

Once the pH is lowered for UF or MUF resins, they start to cure with the application on the wood surface. However, the properties and rates of room temperature curing are too slow to make this a commercially viable process, except for the cases of cold bonding activities at carpenter's shops. Thus, these products are heat cured, with temperature and time being controlled for the optimum cure, which are adhesive formulation and wood product dependent. Caution needs to be taken with aminoresins in that there are certain curing conditions for maximum strength, and excessive heating leads to loss of strength performance. Another problem is that too high of a steam pressure in the product at the end of the press time can cause immediate delamination [145, 146]. Latent acid catalysts, including ammonium nitrate or sulfate, are often added to the adhesive just prior to the application to the wood, in order to avoid process restrictions due to the limited pot life. Ammonium chloride is not used in Europe due to dioxin formation during fires, and the nitrates can be a risk for explosive decomposition at high temperatures. During the hot pressing, these latent acids decompose by reacting with the free formaldehyde of the resin producing ammonia-formaldehyde products and forming either nitric acid or sulfuric acid to accelerate the cure. This process forms a strong bond right out of the press. Resins such as ULEF-UF are not as robust towards variation in operating conditions compared to regular UFs with higher formaldehyde levels due to the low content of formaldehyde and the excess of free urea. Improvement in operating window and cohesive behavior also at low content of formaldehyde can be achieved by introducing melamine.

The curing of UF and MF resins have been extensively studied to obtain the rates of reaction, including the effect of variables by using the temperature–time-transformation (TTT) and continuous-heating-transformation (CHT) curing diagrams [145, 146]. It is important to remember that rates of reaction are important during the production of the resin and the start of curing, but rapidly lose their importance relative to rates of diffusion because as the polymers become larger and water is lost, the remaining reactive groups are less likely to find one another. Research has also shown that the energy of activation of the reaction of polycondensation for PF, UF, MF, and other resins can be influenced by the presence of wood [160].

While UF, MF, and MUF cure by similar mechanisms with acidic conditions, PF resoles cure under basic conditions and the basic pH is needed to keep the phenolics soluble. Additives like methylal and ethylal have been examined, as well as other options for making the phenol copolymerize to make the PMUF [146].

Morphology and Other Properties of Adhesive

The cured UF and MUF adhesives are rigid molecules due to the backbone of ureas and/or melamines linked through methylene groups, which have very limited flexibility (Fig. 14.14). Although any bismethylene ether linkages allow more backbone freedom for elongation and crankshaft rotation, these linkages are less stable and can lead to more polymer degradation. Given that urea and melamine have multiple reaction sites, the polymers can have branching and cross-linking sites to make the polymers even more rigid. This rigidity leads to bonds where there is virtually no adhesive creep which is very desirable. However, any wood product made from particles or fibers will show product creep and low strength if too little adhesive is used, while low adhesive levels in laminated products leads to delamination.

The lack of flexibility in the backbone makes these adhesives brittle, and the volume shrinkage during curing generates high internal strain and stress that in turn leads to brittle cracking in the adhesives [155]. It has been found that adding a polyamine to the formulation increased the flexibility and bond strength for this type of UF adhesive [161–163]. In addition, incorporation of MF segments into the UF has been shown to enhance the toughness of UF resins [144–146].

Because of the large reduction in the formaldehyde to urea ratio over the years, the performance of UF resins has become somewhat weaker and less robust to process changes [154]. However, the ULEF-UF resins retain many of the advantages of UF adhesives in performance, cost, and ease of use.

Aminoresins have the consumer desirability of being light colored, compared to the dark-colored phenolics; this light-colored property also reduces the visual problems of bleed-through or show-through associated with decorative plywood or veneered particleboard. These resins also do not give caustic burns that can be a problem with phenolics. Like phenolics, certain formulations and bonding conditions favor portions of the adhesives entering the cell wall to stabilize them against swelling and to provide better opportunities for adhesion [140, 164]. These resins have been used widely for interior products, but seldom used for oriented

strandboard, where phenolics (in North America) and pMDI (in both North America and Europe) are the main adhesives used.

Durability in Moisture, Heat, and Decay

Durability certainly influences the type of aminoresin used given that exterior products have to be much more resistant to challenging environments than interior products. While UF works well in interior products, it is not good for applications where products are exposed to high moisture. Although heat exposure is not a problem with UF, the more water that is present the faster the UF bond will break down due to mainly acid-induced hydrolysis leading to lower bond strength [151, 165]. Because the moisture resistance of UF decreases above ambient temperatures, the incorporation of melamine into the UF backbone or the addition of pMDI during application can improve the moisture resistance of UF adhesives [146, 166].

Melamine containing aminoresins provide much better water resistance than UF. In fact, they are good enough for use in exterior wood bonding [144, 146]. There are relatively few comparative adhesive studies on long-term exterior exposure; the most complete study was done at Weyerhaeuser by Caster using 13 adhesives at three US test sites (MS, CA, and WA). In these durability tests, the MF and

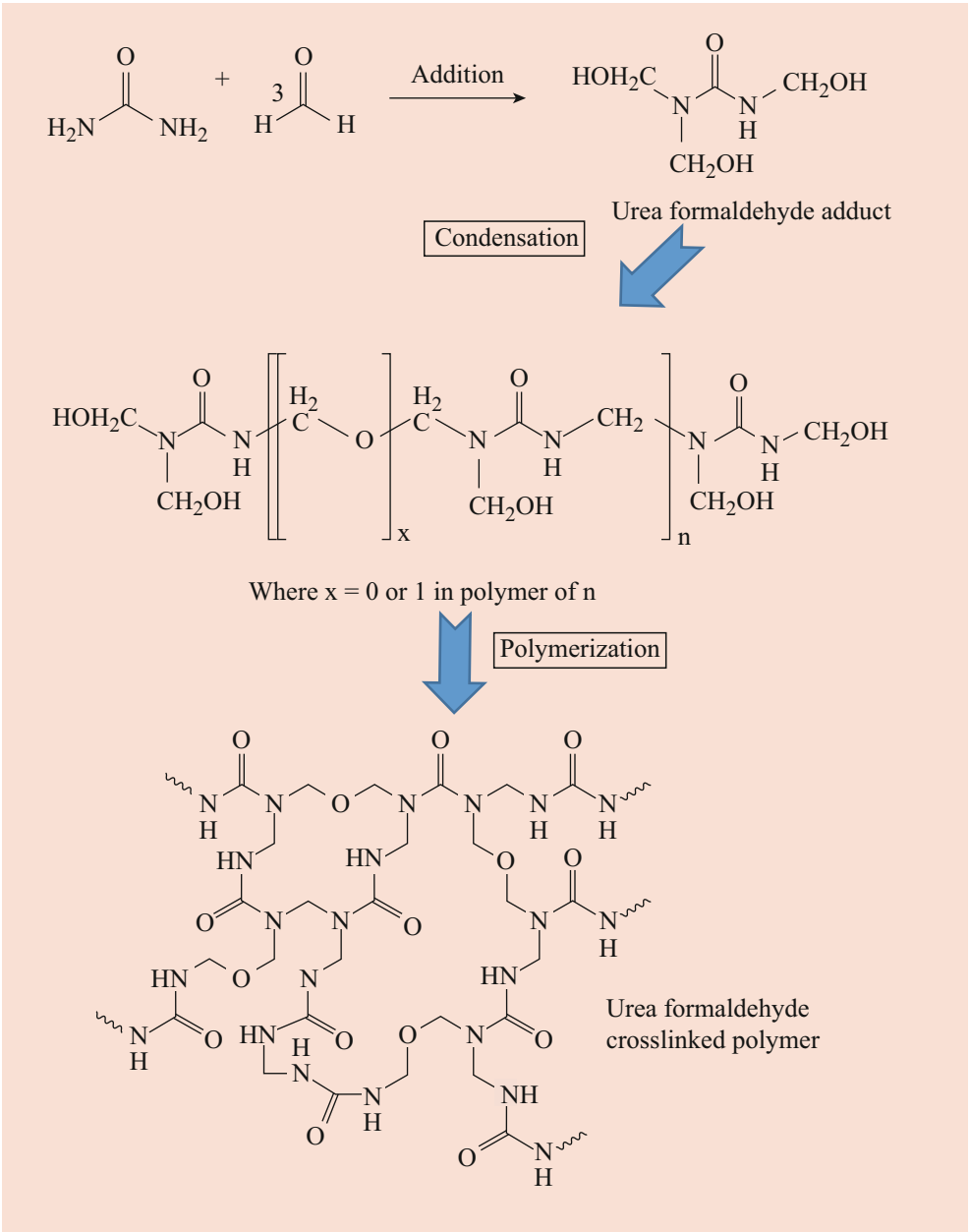

Fig. 14.14 Structure of UF adhesives from starting material to a portion of the final polymer matrix, showing the different types of connections including cross-linking

MUF were better than the UF, but poorer than the PF (phenol-formaldehyde) and PRF (phenol resorcinol-formaldehyde) [167]. Although this is an old study, there has not been any recent studies that are so broad-based, and this research was the basis of the ASTM test D3434 [168].

Utility in Wood Bonding

Of all the wood adhesives, the most widely used are the UF adhesives due to their very low cost, generally good adhesive properties, and their ease of use industrially [106, 144, 145]. However, these adhesives have undergone big changes in formulation since their introduction in the early 1930s [150]. The original formulations had high formaldehyde contents to provide fast and robust bonding and strong adhesives for interior applications [145]. However, formaldehyde emissions have been a continuing problem for UF adhesives because heat and humidity cause the polymer to degrade producing additional free formaldehyde. This has caused practices and standards in different countries to change to have to lower emissions from UF-containing products whose emissions are now even with wood itself, but are not as robust and slower in cure speed [149, 150].

Concern about formaldehyde liability issues has led some companies to use non-added formaldehyde adhesives, PVAc (poly(vinyl acetate)) and PVAx (cross-linked PVAc), pMDI, and soy adhesives. However, most of these other adhesives require process changes for the adhesive user.

Future

With sufficient supply from the widely available raw materials, UF should remain the dominant adhesive for wood bonding. Because of public concern about formaldehyde and the litigious climate, there will be emphasis on other adhesive systems unless an economical way to stabilize the UF to avoid the degradation issue is developed. Some worldwide companies, like IKEA, are looking for bio-based, no-added formaldehyde adhesives because the many different standards and test procedures in different countries make it difficult to produce products that allow a flexible supply chain with the ability to market products that meet public concern around the world [169].

Phenolic Adhesives After aminoresins, the other dominant type of in situ polymerized wood adhesives are the phenolics. Along with formaldehyde, there are two raw materials (phenol and resorcinol) that come from fossil fuel, and two (lignin and tannin) are based upon bio-sources. Because of their good bonding to wood and resistance to degradation, phenolic adhesives are used mainly for structural and exterior applications. These different adhesive types are discussed together because of the similarity in their reactions with formaldehyde to form polymers. The emphasis will be on phenol-based adhesives, which dominate this high-durability market in comparison to resorcinol (very high cost, therefore the wide use of phenol-resorcinol-formaldehyde (PRF) resins), tannin (low availability and high cost), and lignin (low reactivity and inconsistent composition). As is true of most adhesive types, there are a wide array of adhesive products not only for specific bonded wood products but also often for specific mills due to variation in production equipment and operations, different wood supplies, and seasonal conditions.

Chemistry of Adhesive Formulation

Phenolics are made by joining phenol rings together via methylene groups through attachment of formaldehyde and the loss of water occurring in two main reaction steps (Fig. 14.15). The first step is the addition of the formaldehyde to phenolic ring to form a methylol adduct. Then, this adduct is condensed with another phenolic compound to yield a methylene bridge between these two phenolic compounds with the release of water. This process continues to form oligomers and then polymers. These reactions are slow under neutral pH, but are accelerated under acidic or basic conditions [160, 170–172]. However, the novolak adhesive made under acidic conditions is quite different than the resole adhesive made under basic conditions. With the acidic conditions, the first step is slow compared to the oligomerization step so the novolaks are made with insufficient addition of formaldehyde (molar ratio F/P < 1) to stop the oligomerization process, but need added formaldehyde for the curing operation; this makes these adhesives a two-part one. On

Step 1 Methylol adduct

$$HOPh + H_2CO \longrightarrow HOPh\text{-}CH_2\text{-}OH$$

Where HOPh is phenol and H_2CO is formaldehyde

Step 2 Methylene formation

$$HOPh\text{-}CH_2\text{-}OH + R\text{-}NH_2 \longrightarrow HOPh\text{-}CH_2\text{-}PhOH + H_2O$$

Where PhOH is a phenol where the reaction takes place at *ortho* or *para* position to the OH position

Fig. 14.15 The two steps in phenolic synthesis, where the first step is under moderate temperature and basic conditions while the second step is at higher temperature

the other hand, with the basic conditions, the first step is fast compared to the oligomerization; the resoles are one-part adhesives (molar ratio F/P > 1) that only need heat to complete the curing.

The details of phenolic adhesive chemistry has been well described in the literature [170, 173]. The first step is for phenol ring to attack the formaldehyde. In the acidic case, the formaldehyde is protonated, making it more susceptible to attack by the phenol ring. In the basic case, the deprotonation of the phenol makes some ring carbons stronger for attacking the formaldehyde. For the second step, protonation of the hydroxyl group on the adduct makes it easier for attack by the ring carbon of another phenol to form a methylene bridge between phenol groups, while under basic conditions, the negative charge on a phenol makes it better for displacing the hydroxyl group. The strong acids used in the novolak reaction will degrade wood over time even at ambient conditions leading to this type of phenolic not being used in wood bonding. On the other hand, the resole adhesives are compatible with wood and one component oligomers that use heat to complete the cure. From this point on, we will discuss only those phenolics made under basic conditions since these resoles are the ones used as wood adhesives.

Like the aminoresins, this seemingly simple chemistry is not actually so simple, changes in reaction conditions can greatly alter the type of oligomer produced (linear, branched, MW distribution, etc.). Not all the initial links between phenolic groups are methylene bridges. There are some bismethylene ether links as well, but these may be converted to methylene bridges later in the polymerization process by expulsion of formaldehyde [172].

The phenol has three reactive positions: the two *ortho* positions adjacent on the ring to the hydroxyl group, and the *para* position opposite the hydroxyl group (see Fig. 14.16). Due to steric forces, the initial formaldehyde addition takes place mainly at the *para* position. However, certain catalysts can favor the *ortho* position [170, 174]. Similar factors are involved if there is a second or third addition of formaldehyde. Addition at either of the *meta* positions is electronically unfavored. For the chain extension through the phenol molecule, the links may be *ortho-ortho*, *para-ortho*, or *para-para*, making the chain kinked or linear. Another alternative react at all three positions, leading to a branched polymer that could later turn into a cross-linking site. Not only will these variations result in cured polymers of different mechanical properties, but should also alter the rheology for PF oligomers at a given MW.

For the reaction, the basic conditions are usually generated using sodium hydroxide, although potassium hydroxide and ammonium hydroxide can be used. Even though the process is very exothermic, heat is needed to overcome the activation energy barriers for the various steps. The starting phenol is

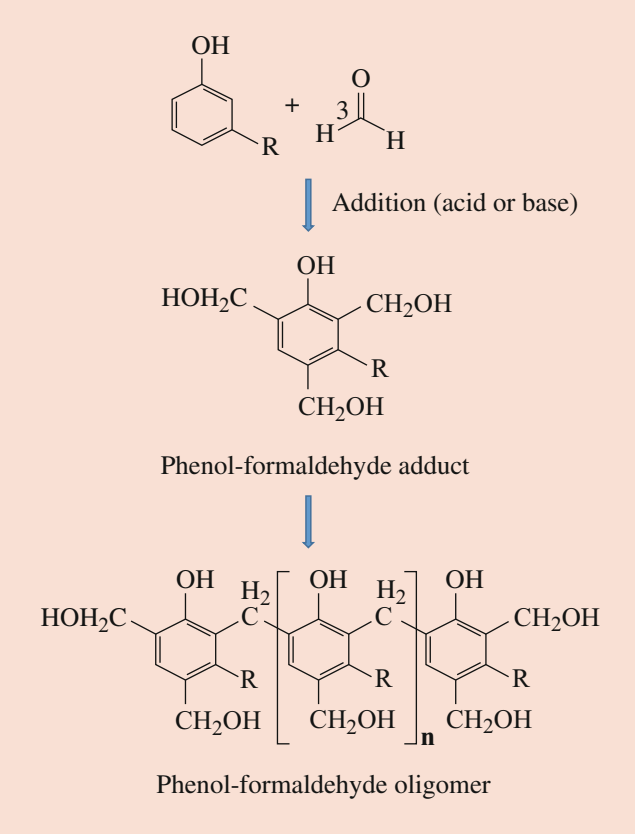

Fig. 14.16 Phenolic reactions from formaldehyde addition to polymerization

quite soluble under these initial conditions, but as the oligomerization progresses, the viscosity increases and the solubility of the resin decreases; thus, enough caustic needs to be used to keep the PF soluble.

PF synthesis can be carried out by adding phenol to water containing formalin (consisting of 37–50% formaldehyde or paraformaldehyde in water) in molar proportions of P:F between 1:1.1 and 1:2.5 [160, 170, 172], but for safety reasons, it is best to start to mix the phenol with part of the caustic and to add the formaldehyde and caustic stepwise to control the exothermic heat generated by the reaction. The alkaline catalyst (usually sodium hydroxide) is added in increments to control the exotherm with mechanical stirring while the reaction is kept between 80 and 100 °C with cooling using a water jacket to control the exothermic reaction. Then, reaction temperatures are allowed to increase between 95 and 100 °C and held there until the required viscosity is reached with vacuum or a cooling jacket used to control the temperature. The resoles are then cooled; they typically have a 40–45% solids content and 150–600 mPa*s of viscosity at 25 °C with sufficient ambient stability for 6 or fewer months with cooler temperatures further increasing the storage life.

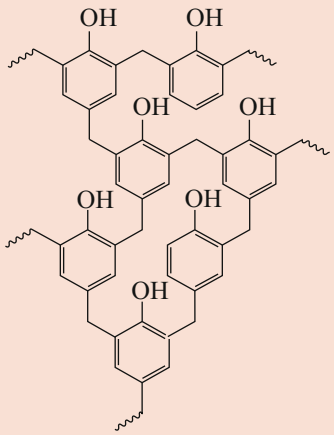

Fig. 14.17 Phenolic structure morphology

Other compounds are available for making phenolics. An important one is resorcinol (1,3-dihydroxybenzene) [170, 175]. Since one hydroxyl activates the *ortho* and *para* positions, two hydroxyls that are *meta* to each other makes the reactions proceed even faster (Fig. 14.17). In fact, instead of the PF reactions requiring heat for condensation, resorcinols (RF) can proceed at room temperature, although mild heat makes the reactions proceed at a more convenient rate. In this case, the site between the two hydroxyl groups is more hindered while the other two sites are of equal reactivity. Thus, resorcinol-formaldehyde (RF) can make adhesives that cure at room temperature, which is very useful in making glulam and laminated veneer lumber, which are hard to heat due to wood being a good insulator. However, resorcinol is much more expensive than phenol; thus, although RFs are used commercially, phenol-resorcinol-formaldehyde (PRF) is much more common. The process of making RFs is similar for making a PF adhesive, with the exceptions that the formaldehyde needs to be limited to avoid the undesirable complete cure during the resin production and that the reaction temperatures are lowered for adding the resorcinol. Thus, resorcinol adhesives are novolak type, making them two-component adhesives with the formaldehyde hardener added just prior to application to the wood. Of all the ways to combine the three ingredients for making the PRFs, an effective approach is for the PF portion to be made first, then the resorcinol is added to cap the PF chains when using a final deficiency of formaldehyde to phenol and resorcinol [170, 175]. This minimizes the amount of resorcinol required but keeps the high reactivity based on the resorcinol end groups, as soon as a formaldehyde source is added for initiating the curing step.

Of the two types of natural phenolics that are used in wood adhesives, lignin is by far the lowest cost phenolic and is a very abundant component in trees and other plants. However, lignin suffers from two major problems: low reactivity and great variability of composition for making adhesives. The low reactivity is mainly influenced by a limited number of free 4-hydroxyl (phenolic) groups on the aromatic rings and the methoxyls at the 3-position (softwoods) or 3- and 5-positions (hardwoods); the 4-hydroxyl group is commonly linked to the β-position of an adjacent hydroxycinnamyl group to make a β-aryl ether. The limited number of reactive sites on the aromatic rings has hindered the use of lignin as a phenol substitute in PF resins. The low reactivity has led many to consider lignin to be a filler more than a coreactant in the formulation of phenol-lignin-formaldehyde (PLF) adhesives. Despite the very large number of papers on lignin sources, purification, and modification [176–182], there has been limited in-depth review of the PLF chemistry in relation to adhesive performance. There are a number of ways to carry out the reactions to incorporate lignin into PF creating PLF [182–187]. With the desire to use more bio-based materials and the availability of new lignin sources, much more research is being done on PLF and other lignin adhesives, as well as some limited commercial applications. The many articles on valorization of lignin have not been very helpful in defining the past and leading to specific chemistry for the pathway forward [188–192]. The use of lignins including purification and modification has not been related to an economic analysis comparing them to using phenol.

The other main bio-based material for phenolic replacement has been tannins, which are the opposite from lignin in that they are very reactive, limited in availability, and higher in cost. Many ways have been developed for making tannin-containing adhesives, and some of these have been commercialized [178, 193]. The hydrolyzable tannins are mixtures of phenols such as pyrogallol and ellagic acid and of esters of mainly glucose with gallic and digallic acids that can provide phenolic molecules for replacement of phenols in PF resins, but require substantial purification. However, the high cost and limited availability of these tannins prevents them from being part of the normal adhesive market.

On the other hand, the condensed tannins have found utility in places where they can be provided locally in good supply and low cost. As with most natural products, isolation from a natural resource and consistency of composition is an issue. However, an advantage of the condensed tannins is that they are more reactive then phenol, and nearly as reactive as resorcinol [178, 192, 193]. Thus, they provide good improvement in cure rates over the phenol, which is again in stark contrast with the lignins that have been discussed earlier. Although the tannins can make good adhesives, the collection and purification of them from natural resources can be an issue. However, there are areas in the world where PFs are

expensive and their instability limits shipment from other parts of the globe. In these places, tannins can have a real market advantage. The many ways of formulating tannins has been covered in detail elsewhere [178, 192–195].

Raw-materials Source and Cost

The main chemicals (phenol, resorcinol, and formaldehyde) are available in pure forms. Formaldehyde as previously mentioned in the Sect. 14.2.2.1. Amino type adhesives is made via a two-step process of forming methanol by a methanol producer and then shipped to an adhesive producer that oxidizes the methanol to formaldehyde as is needed.

Phenol is made from benzene by reaction with propylene to yield cumene, which is then oxidized to yield acetone and phenol by decomposition of the intermediate hydroperoxide [196]. These reactions are relatively clean, reducing the need for any substantial purification of the phenol. Resorcinol can be made by a variety of pathways from benzene, but they are all relatively complicated [197] making resorcinol an expensive chemical.

Most of the lignin produced comes as a by-product from pulping of wood to produce cellulose fiber. The disentanglement process varies considerably depending upon the type of cellulose that is economically preferred [198–200]. Originally, a lot of the market lignin was sulfonated since the sulfite wood pulping process was used previously. These lignins are now used mainly for surfactant applications; thus, other lignins are being intentionally sulfonated to satisfy this market. However, this sulfite pulping process suffers from lack of recovery of the pulping chemicals and environmentally responsible use of the by-products, especially compared to the Kraft process. Thus, the Kraft process using sodium hydroxide and sodium sulfide is the dominant pulping process. Traditionally, Kraft lignin is not separated from the black liquor due to the small market for the purified Kraft lignin, and due to the advantage of burning black liquor for energy and chemical recovery in a recovery boiler with subsequent processing to convert the inorganics back into pulping chemicals. Two basic types of Kraft lignin are available: the traditional lignin produced by full acidulation and the newer partially acidified lignin produced by the carbon dioxide acidulation [201]. Lignin can also be isolated by supercritical extraction, steam explosion, and other methods [188, 190]. Reports exist of lignin being used commercially in a wood adhesive as a phenol replacement in PF, yielding a phenol-lignin-formaldehyde (PLF) [179, 182, 185, 186, 188, 189]. However, the amount and type of lignin being used currently is not always specified, as to whether it is from full or partial acidification of Kraft black liquor and if the original wood is softwood or hardwood. Another type of lignin is the lignosulfonates, which have not been tested much as a wood adhesive [202].

Because tannins are specifically isolated for their chemical utilization, their use as a wood adhesive is better ascertained. In addition, tannins have been used for a very long time, e.g., tanning of leather, and there are many sources and processes for extraction and application; the listed citations provide a better understanding of the variety of materials available and their chemical reactivity [203–205].

Chemistry of Cure with Conditions and Interaction with Wood

The PF resoles have a limited storage time of a few months depending on conditions. Cooler storage temperatures are better for avoiding significant increases in viscosity with time that can reduce adhesive performance. These one-component adhesives only need heat to cure after application. Although a pH above 9 helps to accelerate the rate of curing, the rate of acceleration slows down and can even decrease at pH of 12 and above. The basic condition facilitates the reaction of an activated phenol ring with a methylol group on another oligomer [160, 170, 171]. However, if all the phenols are negatively charged, then the process is less accelerated. The higher pH of some formulations may be more for opening the wood structure to the adhesive and forming a better interlocking structure or improving phenolic solubility, but these aspects have not been studied closely. The curing temperature of the PF adhesives is often above 140 °C requiring high platen temperatures. This higher curing temperature is a disadvantage of the PF compared to other adhesives, such as the aminoresins. Some commercial formulations have been improved to lower this temperature, including increasing the PF molecular weight and adding UF to bring down the viscosity (PUF), adding catalysts, etc. [170, 206–208].

At a certain point, the focus on the polymeric and strength properties of the adhesive becomes more important [109, 143, 170] than the specific chemical reaction sites and rates. This changes the adhesive evaluation methods to measuring the gel point, the cure rate of general chemical reactions using differential scanning calorimetry (DSC), mechanical strength (for example, differential dynamic mechanical analysis (DMA), torsional braid analysis (TBA), thermogravimetric analysis (TGA), automatic bond evaluation system testing (ABES), and dielectric analysis (DEA)). Diverse methods provide different results because each measures a different aspect of the cure process form chemical reactions to rheology to mechanical strength. The curing of PF resins has been extensively studied to obtain the rates of reaction, including the effect of variables, and temperature–time-transformation (TTT) and continuous-heating-transformation (CHT) curing diagrams [160]. For fully cured samples, the PFs stay rigid even when soaked in water, which provides them with good strength under wet tests compared to other adhesives. Given

the rigidity of phenolics, they must also have strong adhesion to wood to prevent fracture from occurring as the wood swells and shrinks.

The reactions that are occurring in the glueline (adhesive layer between the two wood surfaces) can be dependent on many variables such as adhesive formulation including accelerators and metal catalysts, pH, additives such as urea, temperature, time at temperature, wood species, wood MC, as well as the type of bonded product being made [106, 109, 115, 143, 160, 170, 175].

The curing conditions can be more critical for heat-activated adhesives, such as PF, PLF, or tannin, compared to the two-component, room-temperature curing adhesives like RF or PRF. Because phenol and resorcinol are pure chemicals, a good degree of consistency in the curing process is likely. This is not true for tannins and is especially not true for lignins. While tannins are the main products of their different isolation processes, most lignins are by-products of paper production and come from many types of trees processed at different times of the year leading to quite a variation in lignin [209]. In recent years, a great emphasis has been placed upon using lignin and tannin as commercial wood adhesives by themselves or with other chemicals, but the proper formulation and right chemistry are needed to obtain suitable cure rates and properties.

Morphology and Other Properties of Adhesive

Cured phenolics are rigid molecules because the rigid phenol rings are linked through methylene groups, which have limited ability to move, and the cross-linking intensifies this factor as indicated in Fig. 14.17. This morphology gives the phenolics many of their distinct properties. The rigidity of the network in well formulated and well bonded, stable phenolic products creates resistance to creep, which is critical for structural products, even at elevated temperatures for fire resistance.

Part of the good performance of phenolic resins comes from the excellent resistance of the phenolic ring to destruction under normal conditions by oxidation, chemicals, and biological attack. Phenolic resins are relatively stable up to about 200–250 °C before charring, although oxidative degradation can occur under specific conditions at the methylene bridges to produce substituted dihydroxy benzophenones [160]. This is important given the requirements in North America for the adhesive to pass fire tests, where the adhesive needs to resist high temperatures [210].

This heat durability along with high moisture resistance leads to PFs being considered the ultimate in wood adhesive performance for most testing conditions. This also may be why high levels of low reactivity plant proteins and lignin can be added to PF and still meet the minimum bonding standards, as is seen in the work on soy-PF [211].

It should be noted that not all PF adhesives behave the same because of the formulation and bonding variables. It is important that the adhesive develops good intimate contact with the wood for a strong connection to the surface and repair of wood surface damaged during preparation. Nearn stated that sufficient low-molecular-weight components in the PF were important to bond moisture resistance [212, 114]. Although this seems reasonable, and different MW PFs have a different effect on cell wall properties [213, 214], this concept has not been fully proven. The characterization (rate of chemical cure, rate of strength development, etc.) and properties (interaction with wood surfaces, durability of bonds, etc.) of different PFs have been reviewed [215–224].

There can be a range of adhesive bond cure especially in particulate composite cores, which usually have lower wood density, higher moisture levels, and cooler temperatures in the core layer compared to the face layers, making the PF less suitable as a core resin than as a face resin. Wood moisture can also be a problem, since the water dilutes the PF causing greater flow away from the surface; this dilution is compounded by polymerization causing additional water to be produced. One way to address this is to use a higher MW PF (more advanced) resin in the core and a lower MW in the surface layer to get comparable cures. The issues with slow curing PFs in the core of particulate composites has been a strong incentive for replacing the PF with the pMDI adhesives in OSB (in North America) or with MUF in PB (in Europe).

Although the slow cure can be a problem in multilayer exterior plywood products, the durability of the PF has been a very positive factor. While particulate composites require a PF of low viscosity (hundreds of mPa*s) for sufficient spraying and distribution of the resin, a high viscosity PF (thousands of mPa*s) with fillers and extenders has been commonly used for exterior plywood to bridge the wood surfaces [174].

Durability in Moisture, Heat, and Decay

The stability of the chemical link for incorporated formaldehyde is much higher for all the phenolics compared to the aminoresins, making formaldehyde emission negligible in comparison. In some countries, most phenolics are considered akin to a no-added formaldehyde in the final products, but a poorly made phenolic can still have emission issues in the manufacture of the bonded wood product.

The phenolic structure of cured PF adhesives is fairly hydrophobic due to the lack of many polar groups and the low accessibility of the few hydroxyl groups, but the high caustic content can make the bondline more water sensitive. The adhesive shows little drop in strength under wet

conditions compared to dry conditions, which is distinctive from most adhesives. The exceptional durability of PF bonded products towards wet tests has been attributed to the low-molecular-weight components infiltrating and stabilizing the cell walls [214]. To determine durability under severe conditions, a boil-dry machine was developed [225], and it was shown that, of all of the adhesives tested, the hot press PF and PRF lasted many more cycles than other adhesives without losing high wood failure [226]. A study undertaken by Caster showed that phenolics performed similar to wood under this accelerated test and exposure at three outdoor sites, and the reduction in strength of all adhesives was quite similar between the accelerated and outdoor tests [167]. Although PF, PRF, and RF have been shown to be very durable, similar data is not available for PLF and tannin adhesives.

With the high aromatic content and reactivity for tannins, they are expected to have similar heat and decay resistance that the PF, PRF, and RF have. On the other hand, native lignin has aliphatic sections, which should be more susceptible to oxidation and other chemical changes. The various processes for isolating lignin most likely cause changes in the lignin structure and adhesive morphology [190], so the durability of various PLFs could be quite different from one another, and much less than that of PFs, especially moisture durability.

Utility in Wood Bonding

Phenolics are used mainly in exterior and structural applications in North America, but MUF and/or pMDI are often used in Europe in these applications. This is because the somewhat lower durability of MF and MUF has sometimes been considered a problem in the United States. Despite the dark color and higher cure temperatures, the great durability of PF, RF, and PRF provides some advantages over aminoresins and polyurethanes. The use of these adhesives includes all types of beams (glulam, laminated veneer lumber, oriented strand lumber, etc.) and panel products, including OSB, exterior plywood, and particleboard. A problem with the phenolics is their slower cure compared to alternative adhesives leading to longer press times.

Although tannins can provide good adhesive performance, their limited availability, lack of distinct properties, and cost disadvantages have limited the growth of tannin adhesives. Research, especially by Pizzi, has provided many ways of using the tannin adhesives [178, 193, 195, 227–229].

Lignins have cost (if not much purification and modification are required) and availability advantages, being mainly a by-product of cellulose fiber production and normally having fuel value, but they have had a spotty history in wood adhesive use [178, 230]. However, with the emphasis on bio-based material and the new technology for isolating lignin that provides a benefit for companies that pulp wood using the Kraft process, lignin adhesives are entering the market as wood adhesives again [188, 231, 232].

Future

The use of adhesives made from phenol and resorcinol with formaldehyde has a long successful history for providing durable bonded wood for structural and exterior purposes. These adhesives were refined in the early years to provide quicker cure at lower temperatures and improved adhesion for difficult-to-bond wood species. However, there does not seem to be any significant new technology for improving or replacing PF, PRF, and RF, except for in the case of pMDI and PU; so they are expected to keep many of their varied uses in North America.

Although tannins can replace some PF type of adhesives [178, 193], their limited availability makes them a specialty replacement only in certain locales. Although lignin is widely available in large quantities, the various pulping and extraction methods make very diverse lignin types with different reactivates; thus, at this time, lignin adhesives need to be considered as specialty products, if lignin is used as sole adhesive, or used as raw material to replace part of phenol in a PF resin. Consequently, finding a way to provide a highly reactive lignin of consistent properties in large quantities should enable to use lignin as adhesive and hence to establish some industrial use of lignin. Much more emphasis has been placed on lignin research in recent years than in past decades [178, 188, 190, 198, 199, 233].

There has been replacement of PF adhesives with some other adhesives, such as pMDI, for the OSB core adhesive and in some cases the only adhesive in OSB due its lower curing temperature, higher possible production speed, and lower sensitivity to high wood moisture contents. In the case of cross-laminated timber, PRF adhesive is used along with MUF, EPI (emulsion polymer isocyanates), and PUR adhesives [234–236]. MUF has been used instead of PF in OSB in Europe, but currently pMDI is dominating in European OSB production.

Diisocyanate Adhesives

While protein adhesives have been used since ancient times, and UF and PF were developed in the early twentieth century, isocyanates are a relatively new wood adhesive product. When polymeric methylene diphenyl diisocyanate (pMDI) was proven effective for particleboard manufacture in the early 1970s, a new class of wood adhesives was started [237]. The diisocyanate adhesives are very different from

almost all other wood adhesives in most respects. They are nonaqueous liquids with low surface energy allowing them to wet and flow over and into most wood and plant fiber surfaces [238, 239]. Under dry conditions, they can react readily with amino and hydroxyl groups, but need water to self-cure to form the glueline between the wood surfaces [240]. Another aspect is that the isocyanates are a significant airborne hazard even on the laboratory scale, so proper ventilation and personal protective equipment are needed during the wood bonding process, but after complete curing the hazard disappears. Since pMDI is about twice the price of a PF adhesive, panel manufacturers needed to be convinced that the cost was not a significant issue since only half the amount of adhesive was needed compared to PF [106, 143].

Chemistry of Adhesive Formulation

Isocyanates, despite their health hazards, are very important intermediates for making a wide variety of products. The reactivity of diisocyanates provides the ability to react with alcohols to provide polyurethanes, another important class of wood adhesives (see Sect. 14.2.2 Phenolic Adhesives) [241, 242]. Compared to other wood adhesives, the pMDI formulations are quite simple. A controlling factor is the amount of diisocyanate in the pMDI [238]. Since the pMDI also contains oligomeric MDI structures, the amount of polyisocyanate versus monomeric diisocyanate controls the adhesive viscosity and its penetration as well as the adhesive reactivity.

Much of the compositional variations are produced early in the diisocyanate synthesis (Fig. 14.18). The main process is to make the methylene diphenyldiamine (MDI), but some multi-condensations take place to provide polyamines. The mixture of amines is then converted to a mixture of isocyanates. After distilling off most of the MDI, the residue is the pMDI adhesive with about a third of the formulation being MDI. While this residue is in limited volume compared to the MDI, its use in making pMDI adhesives is a good way to provide greater value for the residue.

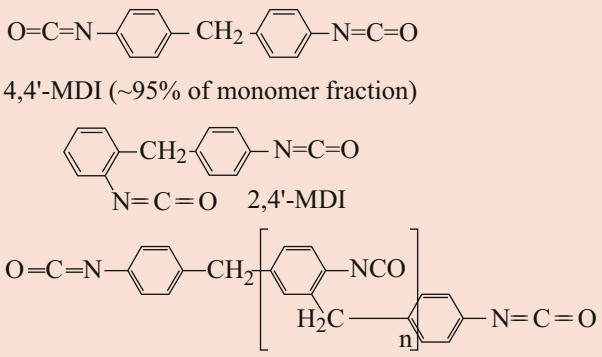

Fig. 14.18 Composition of MDI including the pMDI portion

"The pMDI wood binders have typical molecular weights of 255 to 280 g/mol number average, and 470 to 550 g/mol weight average with viscosities of approximately 0.175–0.25 Pa s (175–250 cP)" [238]. With pMDI surface tension of approximately 41–46 mN/m, they work well in bonding particulate wood composites, such as OSB, PB, MDF, etc., and in bonding especially waxy plant material, like wheat and rice straw. The di- to polyisocyanate ratio is a main factor in the adhesive properties because few additives are added to the pMDI, except for in some cases hindered amine or certain metal salts to accelerate isocyanate reactions [239].

Raw Materials Source and Cost

Benzene is nitrated with a concentrated mixture of nitric acid and sulfuric acid at 50–60 °C to yield nitrobenzene. This is then reduced with hydrogen and a catalyst to yield aniline. To convert aniline to multiple function amines, it is reacted under acidic conditions with formaldehyde [243, 244]. The preferred product is the linear 4,4′-methylenedianiline, but the 2,2′- and 2,4′-dianiline are also formed, as well as various oligomers (which were then the reason to call the final product called polymeric, but it is only a multifunctional isocyanate and not truly a polymer). After the neutralization, the amine mixture is treated with phosgene in an aromatic solvent to produce the isocyanate mixture. Removal of the solvent and most of the preferred 4,4′-MDI by distillation leaves the residue with a certain proportion of the monomeric MDI and the polymeric material, with the mixture sold as pMDI. Although the production process may be altered to make somewhat more pMDI, the market for MDI has a big effect on the pMDI availability. Although the raw material is the inexpensive benzene, the number of complex reaction steps results in a high cost for this adhesive even with large-scale commercial production. There is also variability in cost since it is a by-product, and there are a limited number of suppliers.

Although the chemistry and resin composition seems straightforward, the adhesive formulation is somewhat more complex. Rheology is important for pMDI because it is necessary to control both the spread on the wood and the penetration so that the adhesive is in the right place for good adhesion to the wood and to form a network between the wood surfaces.

Chemistry of Cure with Conditions and Interaction with Wood

The isocyanate adhesives are quite stable materials unless they come into contact with a group that has active hydrogen (H_2O, ROH, RNH_2, RSH, etc.). Primary and secondary amines are typically most reactive, followed by primary alcohols, water, secondary alcohols, and phenols in that general order. Carboxylic acids and amides are the least reactive with isocyanate [238]. However, in normal wood bonding, the water is accessible in much greater molar ratios than other reactive materials, leading to this being the predominant reaction. Reaction with water is very important for developing the adhesive's cohesive strength [238]. When the isocyanate reacts with water, it first forms a carbamic acid, which is unstable and decomposes to an amine and carbon dioxide [238], see Fig. 14.19. The amine can then react with another isocyanate to make a urea structure, building up stepwise to a polyurea. With the pMDI containing polyisocyanates, cross-linking is likely to occur. There are also the reactions of isocyanates with the ureas to form a biuret for increased cross-linking. The carbon dioxide formed in these reactions results in gas bubbles in the adhesive film, but these have not seemed to hinder the good adhesive strength, even offering some gap filling performance.

An important aspect for curing isocyanates, whether it involves pMDI or one-component reactive polyurethanes, is that the adhesives need moisture to cure. Thus, the pMDI reacts well with wood that has sufficient or elevated moisture content, while other adhesives do not, but develops strength slowly with very dry wood. Bonding may be a slow process with fully acetylated or heat-treated wood due to their limited moisture content. After the initial reaction, the bond can require up to a week of conditioning to develop full strength; testing, especially wet testing, too early can give low strength values.

Morphology and Other Properties of Adhesive

As an organic liquid adhesive, the pMDI wets the wood surface and subsurface better and more efficiently than the typical waterborne wood adhesives, allowing it to bond the wood surface and to repair damaged wood cells. This may be why the pMDI can be used at half the amounts as the other adhesives. It penetrate the lumens well without wasting adhesive by only coating the lumens [127, 245, 246], but how well it infiltrates wood cell walls is not clear according to different reports on the issue [124, 238]. The best available data indicate that the pMDI under typical bonding conditions does not react with the cell wall polymers (carbohydrates or lignin) [124, 247], most likely due to easier access to water and faster reaction with water than the cell wall polymers. However, it is possible that they form interpenetrating polymer networks with the wood cell walls [130, 248].

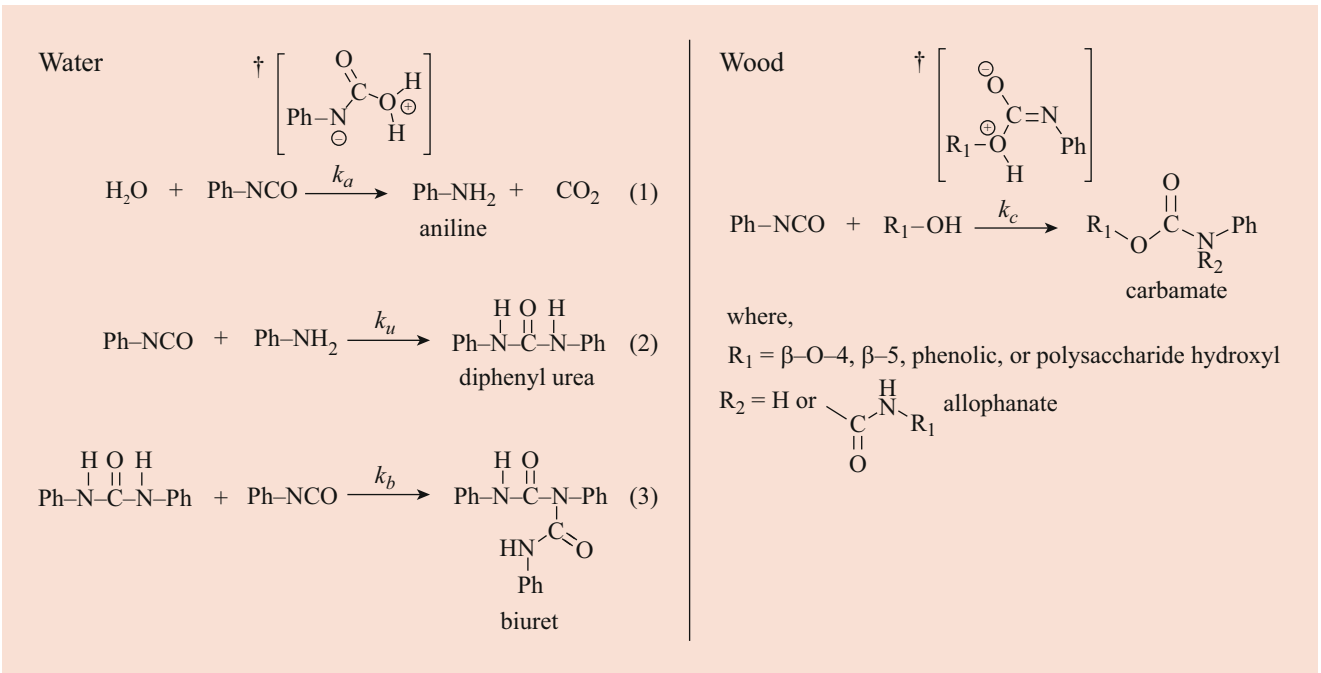

Fig. 14.19 Illustration of isocyanate reactions with wood versus self-curing using a monoisocyanate for simplification, but the commercial adhesives have multiple isocyanates having the same types of reactions, providing a polymeric structure. The † indicates potential intermediates. [124, 234]

The good wetting of surfaces makes pMDI adhesives excellent for making composites because of increased adhesive bonds between surfaces, rather than the spot welds obtained with aminoresins and phenolics. The pMDI works well in the core layer of particulate panel products because it cures well at lower temperatures and higher moisture levels. On the other hand, it is less useful in the face layers of these products because their specific properties are less advantageous and pMDI adheres to the pressing platens if a release coat is not applied to the platens. In addition, these pMDI adhesives do not have tack for holding the panels together prior to curing. The fast penetration of the pMDI is a disadvantage for laminates because there is little holdout for transfer of the adhesive to the adjoining wood surface and bridging between rough surfaces; therefore, it is not used in these applications.

Normally, the pMDI is applied in its viscous liquid form. If mixed with water, then it needs to be emulsified in the application plant since its pot life is less than 5 h [239]. It can also be combined with other adhesives and make emulsion polymer isocyanates and polyurethanes [238].

Durability in Moisture, Heat, and Decay

Because the pMDI is not useful for bonding laminates, which are used in the most common methods for testing adhesive durability, there are limited ways of comparing the durability of these adhesives to most other wood adhesives. However, the durability of the pMDI-bonded particulate composites does show the good adhesion and cohesive strength of these adhesives. The pMDI-wood binders are labeled as highly durable exterior grade adhesives surpassing the UF and the more durable MUF binders which did not receive this designation [238]. Polyureas formed during curing have high hydrogen bonding capacity, along with excellent thermal and hydrolytic stabilities. Consequently, polyurea networks should adhere strongly to wood through secondary bonds, apart from other interactions, such as hydrogen, polar, and dispersive bonding, and mechanical interlock.

Utility in Wood Bonding

The pMDI adhesives are excellent for particulate composites (particleboard, fiberboard, oriented strandboard) because of their low viscosity and surface tension for good dispersing on wood surfaces. Their low surface energy means that the droplets spread over the wood surface and penetrate through the surface, and their good cohesive strength holds the particles together after curing. However, with limited polymerization, the uncured adhesive does not have sufficient molecular weight or moisture to provide the tack needed for holding the particulate mats together. In addition, their good adhesion to materials other than wood means the cured adhesives in the face layer bond to the platens unless release coatings or agents are used on the platens. Their low sensitivity to high MCs and low cure temperatures make them more effective as core adhesives than face adhesives. They also seem less sensitive in their cure to fire-retardant chemicals than do some of the formaldehyde adhesives for fire-retardant boards. The high penetration with low hold out and sensitivity to low moisture conditions make them less useful in overlay applications compared to aminoresins and phenolics.

The pMDI adhesives also bond well the agrifibers that can have waxy coats, which is a problem for the waterborne aminoresins and phenolics [249]. Given their high adhesion to non-wood surfaces, isocyanates are also useful in bonding wood to non-wood materials such as metals, fiber-reinforced plastics, glass, and concrete.

Future

The use of pMDI should continue to grow with the continuing emphasis on the commercially important particulate composites, which are a very efficient use of the wood resources. As a by-product of the MDI production, the supply of pMDI is somewhat limited and depends on the market situation of other products generated out of isocyanates, especially foamed products. The pMDI is less likely to make its way into laminated products which are already served by formaldehyde resins and polyurethane adhesives, and where it can have problems bridging between the surfaces.

Epoxies

There are other in situ polymerized adhesives, but none of them except for epoxies have developed any significant market, other than those for home use and specialty applications. Other in situ polymerized adhesives are the acrylates, used especially in the electronics industry, anaerobic, structural acrylic, and cyanoacrylates.

Epoxies are very commonly used for bonding, coating, and potting a wide variety of surfaces from plastics to metals and concrete. They, at one time, received a lot of attention as wood adhesives because of their structural strength, normal durability, and gap-filling abilities, but were unable to pass the more severe water resistance tests [250, 251], except for the studies by Caster [167, 252]. They are easy to use for repair of delaminated wood joints and decayed wood products and for gap-filling applications, including ship construction and repair. However, they were never by themselves able to reach the level of exterior durability required for bonded structural wood products.

Chemistry of Adhesive Formulation

Epoxies can self-cure under a few conditions, but generally they are very stable until they are mixed with a hardener. The

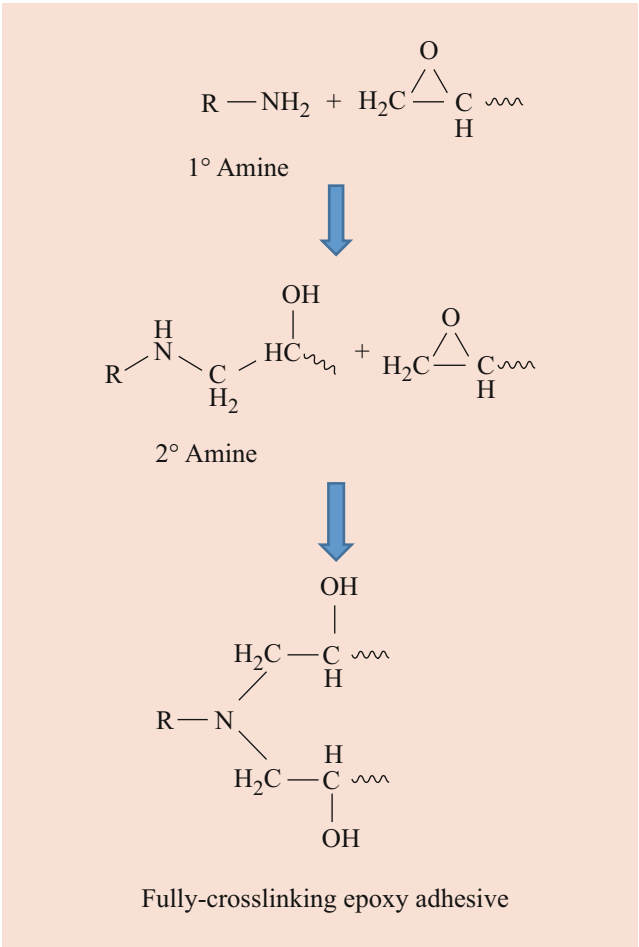

Fig. 14.20 Example of reactions of an epoxy with an amine at a single amine reaction site. Usually polymers are made using a difunctional epoxy and a polyamine

hardener can be a number of functional groups including the commonly used aliphatic polyamines and polythiols for quick-setting epoxies. In Fig. 14.20, a typical epoxy is illustrated with its curing with an amine hardener.

Although there are a wide variety of epoxies and curing mechanisms [253, 254], the ones examined for wood bonding have been two-part adhesives, using a low-molecular-weight bisphenol-A type epoxy, such as bisphenol A diglycidyl ether (BADGE or DGEBA), with a multifunctional amine curing agent; this combination is referred to as a 5-minute epoxy. The DGEBA epoxy is relatively low in viscosity and can produce high-molecular-weight polymers if cured with a diamine. However, the curing agent normally has more than two amino groups in order to provide a cross-linked network that is a very strong adhesive or coating for rigid materials. The process for making DGEBA can also make higher molecular weight version of this epoxy and when using different starting materials, multifunctional epoxies can also be made. When a flexible adhesive is needed, the components can be altered to provide the needed flexibility by varying the hardener or epoxy structures, especially if bisphenol F (using formaldehyde instead of acetone to link the two phenol rings) is used as the starting material [253–258]. The standard epoxy can be altered in many ways by adding other materials; most commonly it is toughened usually by finely dispersing small rubbery domains to minimize the brittle impact fracture by dispersing the crack into microcrazing. Although no solvent is used with these adhesives, small amounts of low volatility organics can improve wetting.

Raw-Materials Source and Cost

A wide variety of materials can be converted to epoxies by reacting an alcohol with epichlorohydrin and caustic; the most widely used is bisphenol A, made by reacting phenol with acetone to create a diphenol, which is then reacted with epichlorohydrin to yield DGEBA or higher molecular weight diepoxies by further reactions.

DGEBA epoxy is made in two steps, first with phenol being reacted under basic conditions to form bisphenol A, then by reacting epichlorohydrin with the diphenol under basic conditions (as indicated in Fig. 14.21), a standard way of adding epoxy groups [253]. The epichlorohydrin is made from propylene by reaction with chlorine and then dehydrochlorination with sodium hydroxide. For the DGEBA and epoxy products, it is desired to have very low residual epichlorohydrin for health reasons, and for electronics to remove as much chlorides as possible.

Although a number of curing agents can be used, the aliphatic polyamines are ones that have been used the most for wood bonding. The amines are formed by reacting ammonia with ethylene oxide, which is made from ethylene reacted with oxygen using a silver catalyst. In addition to the simplest product of ethylenediamine (EDA), higher homologs are made in this reaction. The diethylenetriamine and triethylenetetramine are commonly used for curing epoxy resins, due to their greater ability to form cross-links and much lower toxicity than EDA.

Epoxy adhesive prices, depending on the formulation, range from expensive (approx. $6/kg.) to very expensive for a wood adhesive [258]. Because of the number of chemical steps (two steps starting with phenol), there does not seem to be a way of reducing this cost. For a bio-based material to work in wood bonding applications, it seems that the backbone would need to be rigid like lignin or tannin epoxy, not flexible nor hydrolyzable like a fatty ester epoxy, where most of the research has been done. Research is being done on epoxies from oilseed fats, but these are very flexible epoxies and are unlikely to be used as wood adhesives [259].

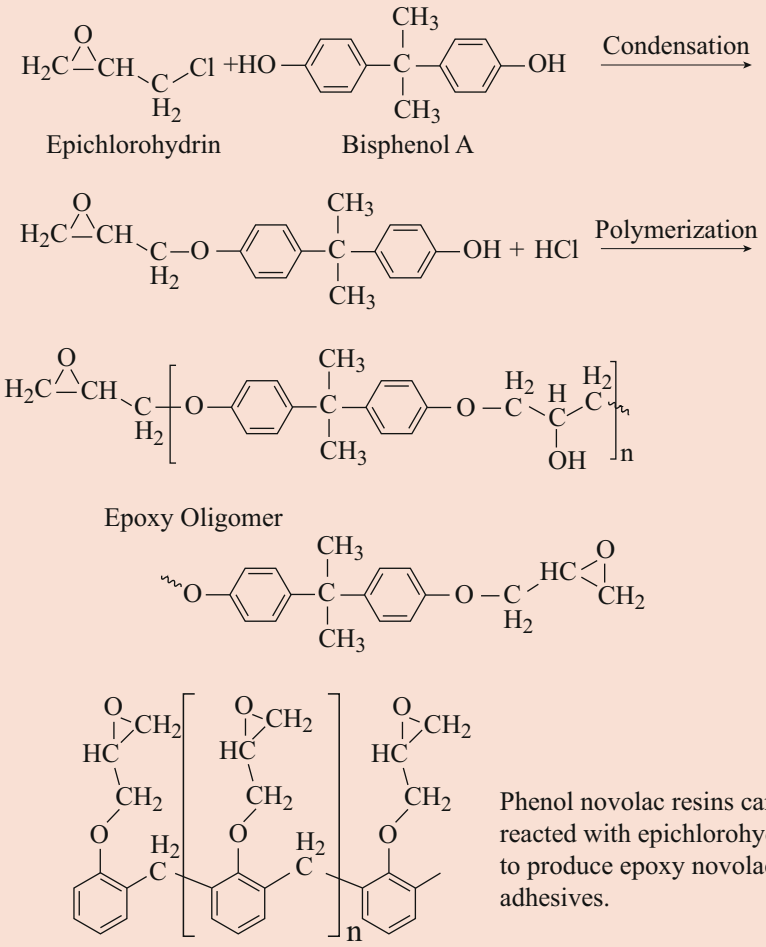

Fig. 14.21 Synthesis of epoxy resins both from bisphenol A and novolac resins

Chemistry of Cure with Conditions and Interaction with Wood

The two components (epoxy and hardener) are very stable until mixed, which has to be done thoroughly because they are not very miscible [260]. At room temperature, the epoxy-hardener reaction starts slowly, but the greater the mass, the faster the rise in temperature due to the reaction being very exothermic. Some "room-temperature curing" epoxies have good initial strength after 5 min, but full cure continues after this. Even greater cure is accomplished by heating the bonded assembly to allow some plastic flow of the epoxy that increases the contact between the unreacted amines and epoxies.

Epoxies are one of the few in situ polymerized wood adhesives that form a decent self-supporting film for mechanical testing. However, there is a concern that the epoxy bond between the wood surfaces is not as strong as the epoxy cured by itself in the dry state [261]. However, good penetration of epoxies into wood lumens has been noted in other research, but they still did not provide good adhesive wet strength [134, 262]. The answer seems to involve the epoxy's limited infiltration of both components into the cell wall to provide the adequate strength development [134, 140]. It can be speculated that the very low polarity of the epoxy resin limits its infiltration of cell walls preventing stabilization of the cell walls towards swelling, while the highly polar hardener infiltrates the cell walls, changing the epoxy/hardener ratio near the interface leading to incomplete curing. There has been little work on improved epoxy adhesives for wood adhesives in recent years, but there may be some ways to improve their bonding performance.

Morphology and Other Properties of Adhesive

Depending on the formulation, cured epoxies can vary from rigid to somewhat flexible solids, although rigid epoxies can have problems with impact fracture [253, 254]. The impact fracture can be addressed by toughening the epoxy through selection of the chemical nature of the two components (see below) or through adding very small filler

particles (reinforcing filler) or well dispersed rubbery polymers. Although there is a vast epoxy adhesive literature, it is mainly related to bonding for aerospace and automotive applications under conditions that are not necessarily helpful in understanding wood bonding [253, 254, 257, 258]. The types of epoxies used in wood bonding are fairly rigid from the aromatic backbone epoxy, the short chains of the linking amines, and the cross-linked structure of the final matrix. The flexibility of the cured epoxy matrix can be increased by having longer chains (aliphatic or aromatic) between the end epoxy groups or using more long chain diamines, both of which make longer chains between cross-links. Many epoxy bonds retain their strength over wide temperature and moisture ranges. This performance and lack of creep shows a rigid network with good cross-linking.

Four real advantages of the epoxies for bonding and repairing wood is that they are gap filling, heat resistant, need little clamping pressure, and they can also have minimal volume shrinkage when formulated with fillers that do not shrink as the epoxy cures [263–269]. The adhesives can be applied in place to an existing structure, which saves a lot of time and money.

Durability in Moisture, Heat, and Decay

Epoxies are normally very durable, as is shown by their use in products ranging from cement coatings to aerospace applications. The durability has also been shown through a wide variety of testing methods on a wide variety of substrates [253, 254, 270]. The range of epoxies and curing agents allows for making a great variety of products to meet specific performance requirements. No one type of epoxy or curing agents can provide suitable properties for all the various applications; however, all cure into cross-linked products with a long lifetime. This cross-linked network with high decomposition temperatures results in sufficient strength to hold airplanes together with the right epoxy and curing conditions.

However, epoxies have problems forming strong and durable bonds to wood, especially under standard wet testing [134, 251, 261, 263, 271]. If an adhesive has good wood penetration, bonding strength, excellent cohesive strength, and great moisture resistance for the epoxy itself, why does it not perform well on accelerated ageing tests bonded wood? On the other hand, epoxies are good wood adhesives if not subjected to fast wood swelling experienced in the accelerated testing [264] or if an effective primer, such as hydroxymethylated resorcinol (see Sect. 14.2.3 Primers) is used with wood [252, 272]. The answer seemed to be the interfacial strain that when sufficient harsh will rupture the adhesive interphase [134, 140, 250].

Utility in Wood Bonding

Epoxies are too expensive to be used in typical wood bonding applications. However, due to their ability to repair decayed wood and delaminated wood, rapid cure at room temperature and their gap filling properties, epoxies will continue to be used in specialty applications. After removing all the rotted wood and reinforcing the surface with a suitable primer, the epoxy can be applied and cured to repair the wood and prevent further decay.

Future

Epoxies will continue to play a minor role in wood bonding. There does not seem to be any other wood adhesive that can be strong, durable, and gap filling, except for polyurethanes. Both epoxies and polyurethanes have moisture durability problems, but this can be overcome by using a suitable primer [144, 254, 273–275]. Although the primers have been effective (see Sect. 14.2.3 Primers), the mechanisms of the different primers have not been unambiguously determined. Some commercial epoxies (like West Systems and Sicomin Epoxy Systems) advertise that they have structural products for marine applications, but no data is available to show that they are structural adhesives for wood building applications, There is considerable work being done on bio-based epoxies [255, 256, 259], although it is not clear how many of these materials are commercially viable and whether they solve the wood-bond durability properties of the epoxies.

Pre-polymerized

The pre-polymerized adhesives are the other major class of wood adhesives and consist mainly of high-molecular-weight oligomers or polymers that may be further polymerized or cross-linked covalently by the addition of reactive molecules. In fact, some of these base polymers serve as polymeric adhesives on their own, such as polyvinyl acetate (PVAc) and proteins. However, further treatment is used to enhance their performance especially at high temperatures or with water exposure. This group contains some of the oldest wood adhesives (proteins from animal sources) and some of the newest ones such as polyurethanes and EPI (emulsion polymer isocyanates), which is an emulsion polymer cross-linked with an added isocyanate component.

Several main differences exist between these pre-polymerized adhesives and the in situ adhesives discussed previously. In the adhesive formulation, the polymers are too large and, in many cases, too nonpolar to infiltrate into the cell walls. Additionally, most of these adhesives are almost totally dispersed in water, rather than being mainly solubilized. These pre-polymerized adhesives are so high in molecular weight that if they were in solution at a useful concentration, the adhesive viscosity would be too high to use. For curing, the main factor is the coalescence of the

dispersed particles by the loss of the water solvent, often with cross-linking of the polymer chain and some chain extension. From a cost perspective, they are about mid-range in cost compared to the in situ polymerized adhesives. For the morphology, the pre-polymerized adhesives have a more linear backbone allowing the cured adhesive to have some flexibility. These adhesives can undergo water plasticization and thermal softening, which is rare for the in situ polymerized adhesives. In the applications, these adhesives are generally not used to make particulate composites, but are used in lamination where there is a continuous adhesive film.

Polyvinyl Acetate

Chemistry of Adhesive Formulation

Polyvinyl acetate (PVAc) is a polymer of vinyl acetate. This standard, so-called white glue, is familiar to almost everyone; its wide use in school rooms and homes is a testament to its safety.

Vinyl acetates chain polymerize using a free-radical mechanism [276–279] by one of several processes. For example, an initiator, such as benzoyl peroxide, is converted into a free radical via heat. This radical then reacts with the terminal ethylene carbon end of the vinyl acetate to form a covalent bond and generates another radical adjacent to the acetate, see Fig. 14.22. This propagation continues, but it slows as the concentration of monomers decreases. At some point, the propagation reaction terminates due to coupling of the free radicals or reaction with a free radical trap. Higher amounts of initiators lead to shorter chains, while too little lead to incomplete reaction. The polymerization process makes a polyethylene polymer with acetate groups at every other position on the chain.

Although this free radical polymerization process can be carried out with or without an organic or aqueous solvent, the most common method for wood adhesive applications is to use a waterborne emulsion [277, 279]. To make these adhesives, a protective colloid (0.05–0.1% of the weight), such as polyvinyl alcohol or substituted celluloses, is added to prevent coalescing of the water insoluble monomer droplets. Using a surfactant and/or protective colloid, the vinyl acetate can be dispersed in water with sufficient agitation. Different PVAcs can be made by varying the amounts of initiator, surfactant, and protective colloid relative to vinyl acetate, along with agitation conditions and temperature [277]. Larger particle-size emulsions are preferred for wood bonding.

Although the formulation of PVAc adhesives sounds straightforward, this is not necessarily the case in the real world. In addition to variables in the vinyl acetate emulsion polymerization conditions, a large number of other unsaturated organics, such as other vinyl esters, or ethylene, can be added to form copolymers with different glass transitions,

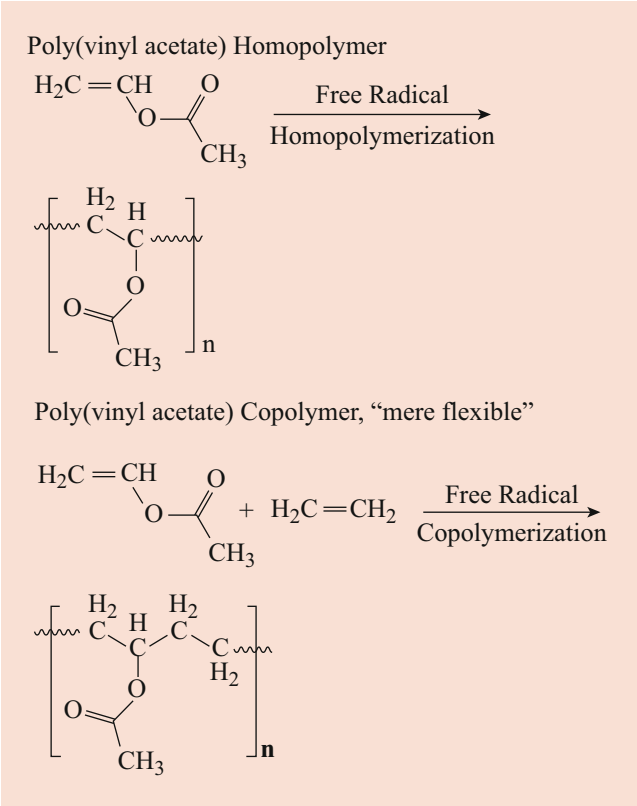

Fig. 14.22 Vinyl acetate free radical polymerization

melting properties, rheological properties, particle coalescence, film flexibility, etc. [276–278, 280]. These emulsions can also be blended with other polymers or added cross-linkers, as discussed below, to provide greater durability, including heat and moisture resistance. Changes, such as increasing the ethylene content to make ethylene vinyl acetate, can be made for better bonding to plastics and increased tack for quick holding power. The lack of a recent encompassing review of PVAc wood adhesives makes a good understanding of structure-property relationship difficult, but the Dunky section on binders in ▶ Chap. 24 of this handbook provides guidance along with searches of the literature, including patents, and examination of material safety data sheet's information to provide additional guidance on these adhesives.

Raw-Materials Source and Cost

The major industrial route to vinyl acetate involves the reaction of acetylene with acetic acid, or ethylene with acetic acid with oxygen in the presence of a palladium catalyst [277, 281, 282]. Another process uses acetaldehyde reacted with acetic anhydride [282]. The acetic acid comes from acetylene and water to make acetaldehyde that is then oxidized to make the acid. The polyvinyl alcohol (PVAl) that is used as the protective colloid for making the PVAc is made by hydrolysis

of PVAc, because the vinyl alcohol precursor is not stable and rearranges to acetaldehyde readily after being made.

The PVAcs are not the lowest cost adhesives, but their ease of use and low toxicity makes them cost effective for wood product assembly, like furniture and cabinetry.

Chemistry of Cure with Conditions and Interaction with Wood

The PVAc is a convenient to use product in that it is a moderate viscosity, high solids adhesive that has a low health hazard, and can be applied to most porous items, such as wood. However, it requires clamping for several hours for the adhesive to obtain enough strength to be handled. As the water moves from the glueline into the wood, the dispersion particles form a film. At below freezing temperature, the film formation does not take place, and the product is a powder. A coalesced film of PVAc is still a thermoplastic and will soften and eventually melt at elevated temperatures.

Although simple PVAcs are single-component adhesives that can bond the wood at room temperature after a sufficient clamping period, some of the modified adhesives, with the addition of a second component (cross-linker), usually need heat to develop full strength of the PVAx. Even in these cases, the PVAc emulsion is the base polymer, so coalescence of the emulsion particles is important for film strength. Some added adhesives, like phenolics or melamine-based resins, can provide a film with a higher melt transition and therefore have more heat resistance, but the adhesive will still soften and absorb water [277, 283, 284]. However, some additives, such as glyoxal, formaldehyde, or isocyanates, as well as complexes such as organic titanates, chromium III nitrates, or aluminum III nitrates provide effective interaction of the PVAc particles [279, 280, 285, 286]. Some of these systems require adding another component, such as N-methylolacrylamide to the adhesive prior to application for cross-linking of the PVAc particles [279, 284]. To prevent confusion, it is important to note that PVA is often used in the literature to describe either PVAc, PVAl, or PVAx. A PVAc with an isocyanate is a PVAx, but if the PVAc is (completely or partially) hydrolyzed to make it a PVAl and mixed with an isocyanate becomes an emulsion polymerized isocyanate (EPI or in Japan API).

Morphology and Other Properties of Adhesive

The PVAc emulsions have two domains in the solidified adhesive. The PVAc domain inside the emulsion generally stays as a sphere and exhibits the properties of the PVAc polymer or copolymer from the polymerization step. The other domain is the water that moves away from the glueline between the two wood pieces as the dispersed particles come together to form a film as shown in Fig. 14.23. This means that the adhesive will soften similar to the pure polymer. Another important part is the interface between the emulsion particles. When PVAl is used as the protective colloid, it is natural that the PVAl is a main part of the interface. This factor plus the normal plasticization of the PVAc means the adhesive has a great sensitivity to high moisture environments [287].

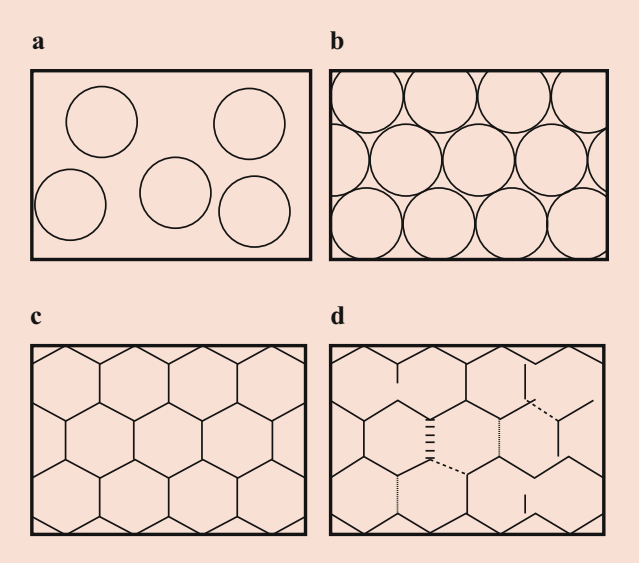

Fig. 14.23 PVAc film formation showing its colloidal nature as the water is removed to provide close contact of the dispersion particles: (**a**) dispersion, (**b**) weak film, (**c**) strong film, (**d**) some merger of particles, (Drawing provided by Prof. Charles Frazier, Virginia Polytech University)

Several different ways have been developed to make the PVAc more durable and creep resistant by altering the PVAc particle interface to form cross-linked PVAc (PVAx). One route is to copolymerize the vinyl acetate with N-methylolacrylamide (NMA) [284, 288]. Crosslinking of NMA can be achieved by thermal curing or by catalysis with acids or bases. Thermal curing is more efficient and generally gives better physical properties [289]. Another route is to add a polymer that can thermally cure, such as a phenolic. Both routes give improved strength at the adhesive droplet-droplet interface by developing covalent bonds across the adjacent droplets [280, 284, 285].

Durability in Moisture, Heat, and Decay

Because the PVAc can absorb moisture and the particles are not fully fused, these adhesives have a fair amount of water sensitivity. This limits the PVAc to mainly interior applications. Being an unnatural polymer, few organisms are available to attack the adhesive, but the use of a biocide solves any degradation problems.

PVAc adhesives are weak compared to other wood adhesives in durability due to their thermoplastic behavior. This has caused problems in the past with some applications, such as the fire resistance of finger-jointed studs. The cross-linked or phenolic-fortified PVAx have reduced the impact of these problems, but have not eliminated totally the thermoplastic characteristics, which affect the moisture and heat durability.

Utility in Wood Bonding

PVAc has been the most common home adhesive for many years and is still widely used in commercial wood bonding. In general, PVAc adhesives have been mainly limited to interior applications, although they have been used in making window frames. The ease of application, the ability to control polymer MW and particle size, the good penetration into the wood structure, the room temperature cure, and the low toxicity are strong positives for the PVAc adhesives. Although not suitable for most structural applications and particulate composite applications, these polymers are good for most assembly operations where the ease of use and safety outweighs their moderate cost.

Limitations of the basic adhesive formulation can be addressed by copolymerization with other unsaturated monomers, fortification with thermally curable polymers like the phenolics, and/or adding cross-linking agents that enhance the range of application for PVAx adhesives.

Future

PVAc adhesives will continue to be used mainly for interior applications. With improved formulations and the ability to replace UF in some laminating applications, the market for these adhesives should continue to grow. However, polyurethanes with their better water resistance have replaced PVAc and PVAx in the home improvement market.

Polyurethanes

Of all the wood adhesives, the polyurethanes (PUR or PU) have the widest variety of components and product properties [241, 290–292]. PURs have good adhesion to a wide variety of substrates and are usually tough polymers. There is some use for thermoplastic PUR adhesives in wood bonding, especially for the hot melt type in product assembly; however, most PURs in wood bonding are thermosets. Thermoset PURs can be generally classified as either two-component (2C), consisting of diisocyanate and diols mixed during application, or as one-component (1C) oligomeric diisocyanate-capped urethane that is moisture cured. In recent years, 1C hot melt polyurethanes have been developed that are also moisture cured and very useful in product assembly due to high green strength. The PURs are also different from most adhesives in that they have soft, mainly continuous domains of the diols or polyols linked to nm-sized hard domains of the short chain polyurethanes and polyureas (from the isocyanate self-reaction after water exposure). This provides a unique character of hard domains for strength and soft domains for flexibility that other adhesives do not have. As well as the type of diol used, the variation of these domain types and sizes provides another formulation aspect.

Chemistry of Adhesive Formulation

A urethane bond is formed from the reaction of an alcohol and an isocyanate, see Fig. 14.24. Thus, a polyurethane is produced when both reactive components have difunctional or higher functionality; the reaction conditions must exclude water to limit self-curing of the isocyanate, which leads to an undesired self-polymerization. Isocyanates react at different rates with groups possessing an active hydrogen, with amines being much faster than alcohols, see Table 11.1 in Ref. [241]. Although the reaction rates with water are about equal to that of alcohol groups, small amounts of water have a large number of moles of active hydrogens that are more sterically accessible than alcohols. Making dry conditions an absolute necessity.

An important part of the PUR is the diol/polyol portion, which can be made from a wide variety of organics with a considerable variation in molecular weight [241, 290, 291]. Oligomerization of alkylene oxides with caustic and a difunctional alcohol template forms polyether diols. Using glycerol as the template leads to triols while sucrose leads to higher functionality polyols and provides branch points for cross-linking the PU chains. These polyether materials have good low temperature properties due to low glass transition temperatures, but are more water sensitive especially when ethylene oxide is used. Typical MWs range from 500 to 2000 for diols and 250 to 3000 for triols [241]. A more expensive, but stronger version is made from polytetramethylene oxides, which has a lower moisture absorption. A low glass transition

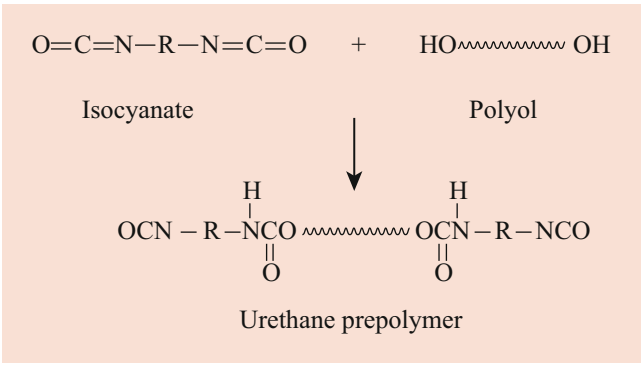

Fig. 14.24 Diisocyanate reaction with diol to form a urethane prepolymer that can further polymerize to form a polyurethane polymer

and low water sensitive polyol is made from oxidation of polybutadiene rubber [291].

Polyester diols can be made from adipic or phthalic acids and glycols. An interesting source for the polyester is from recycling poly(ethylene terephthalate) (PET) plastic bottles [241]. Another polyester source is from oligomerization of caprolactone [241].

The main isocyanates are either methylene diphenyl diisocyanate (MDI) or toluene diisocyanate (TDI) types. However, there are a variety of specialty diisocyanates, such as hexamethylene diisocyanate (HDI), hydrogenated MDI, isophorone diisocyanate, and tetramethylene diisocyanate [241]. Aliphatic diisocyanates are used in coatings because of their light color and UV resistance but are not used in wood adhesives because of their cost.

Raw-Materials Source and Cost

The isocyanates range from slightly expensive to very expensive for making wood adhesives, but they make up only a small fraction of the weight of the product. On the other hand, the polyols are generally less expensive than the isocyanate, contributing to a lower overall cost for the PUR. The main isocyanate is MDI/pMDI, whose source was discussed in the isocyanate section. The adhesives often use the less pure versions of these isocyanates because the objective is not to make very high-molecular-weight urethanes. For example, the MDI can contain the 2,4′-isomer in addition to the main 4,4′-isomer, and can also contain the oligomeric methylene diphenyl diisocyanate. The TDI is made by dinitration of toluene, followed by reduction to the diamine and then reaction with phosgene. It is a mixture of the 2,4- and 2,6-isomers.

The least expensive polyol source is the polymerization of ethylene oxide and propylene oxide as mentioned in the chemistry section. The wide range of polyols and isocyanates and the confidential nature of the commercial wood adhesives negates the value of discussing the source or relative cost of any specific polyol.

Chemistry of Cure with Conditions and Interaction with Wood

An important aspect for curing isocyanates, either for pMDI or 1C PURs, is that the adhesive needs sufficient water after application for curing the adhesive (since no polyols are given in these cases of application). Normally, this is not a problem because, except under very dry conditions, the ambient water in the air and wood are usually sufficient. This need for water to cure is an especially important issue in bonding modified wood, like acetylated wood, which often has low water saturation values. On the other hand, 1C PUR provides the possibility to bond wood with higher moisture content (even green wood). This would hardly be possible for polycondensates (UF or PF) or emulsion polymer adhesives, as they have to get rid of solvent water and water from condensation. In addition, after the initial reaction, the pMDI bond can need up to a week of conditioning to develop full strength, so performance testing should be delayed.

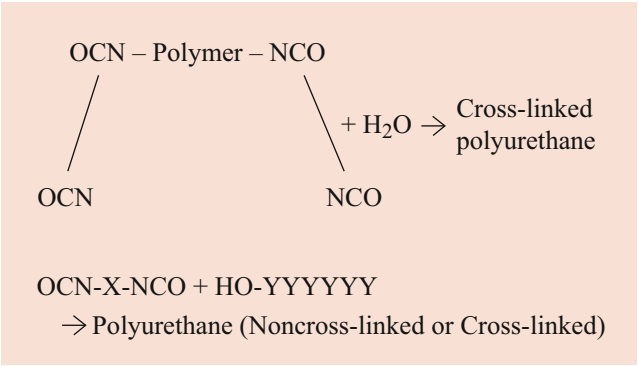

Fig. 14.25 1C and 2C polyurethane with first one involving the reaction of a polyisocyanate polymer with water, while the second is the reaction of a diisocyanate with a di- or polyol (where X is a rigid organic and Y is a flexible organic)

The 1C PURs (Fig. 14.25) are convenient to use for lamination applications in that they are viscous liquids that wet wood and other material surfaces well. Although they can flow into lumens well, they are too large in molecular weight to infiltrate cell walls. These adhesives can work well with some species of wood, but the 1C PUR does not provide good wet strength with ash [293]. However, the use of primers can improve the bond strength and wood failure [142].

For two-component PUR adhesives (Fig. 14.25), the curing takes place upon mixing, and the rate of reaction depends on the reactivity of the isocyanate and polyol, the ratio of alcohols to isocyanates, and the temperature. For good strength, the two components should be well mixed, which can be accomplished by using an appropriate in-line mixer which can handle the ratio and viscosities of the two components. The reaction of the polyol with the isocyanate needs a catalyst, which can be an amine or certain metal salts, such as ferric acetoacetonate and dibutyltin dilaurate.

Morphology and Other Properties of Adhesive

Depending on the formulation, polyurethanes can vary from rigid to flexible, but all tend to be tough polymers. The toughness derives from the hard cross-linked rigid polyurea domains and the soft polyurethane domains (isocyanates reacting with short chain aliphatic diols). These hard domains are linked by soft domains from the longer chain polyols. The hard domains provide strength and stiffness while the polyol domains provide flexibility, impact resistance, and low temperature performance (Fig. 14.25).

The wide range of components and their ratios makes it difficult to draw specific conclusions about different PURs without testing their wood bonding properties. Although polyurethanes can be thermoplastics, the thermosets are much more common in wood bonding to avoid creep under load and at elevated temperatures.

Another feature of the thermoset polyurethanes is the reaction of the isocyanates with water that leads to self-curing cross-linking and development of carbon dioxide bubbles, which do not appear to be a detriment.

Durability in Moisture, Heat, and Decay

In general, the polyurethanes are very durable products leading to their widespread use in adhesives, sealants, foams, and many kinds of solid products. Decay resistance does not seem to be a problem, given their extensive use in sealants. However, heat resistance is an issue with PURs, especially in higher temperature fire testing. The upper temperature limit for retaining wood strength is higher than the typical use temperature of PURs, leading to their decomposition. However, a different opinion exists in Europe where the wood is considered an insulator so that adhesive is not exposed to such high temperatures. According to Clauß, heat stability of polyurethanes is improved by adding an inorganic filler, like chalk, to a high strength 1C polyurethane, but the wood also influenced the results [294]. Wood has different degradation temperatures that produce water and acetic acid mainly from the hemicelluloses that can degrade the adhesive [295].

Utility in Wood Bonding

Polyurethanes have good bonding in lamination applications, including glulam and cross-laminated timber, because the adhesives can rapidly develop appreciable strength with a short clamping time, and then continue to cure at room temperature; they can have set times ranging from minutes to an hour. The ease of application and curing of 1C PUR has made them a desirable product, with the greatest interest in Europe, but cross-laminated timbers have increased the use in the North America [296]. The basic chemical costs of the PURs make them somewhat more expensive, but it is common for structural applications due to higher cost raw materials to achieve the expected performance. In North America, the standards for structural adhesive are high and are tied into building codes that were formulated on the basis of PF often being the standard; thus, this market is more difficult to enter than for other wood products.

Another application is the assembly of final products where the rapid development of strength is less important. These adhesives are used for both interior and exterior applications, growing the use of wood and increasing the lifetime of products under more challenging conditions. An important aspect of the polyurethanes is that they not only bond to wood well but also to other surfaces such as metal, concrete, glass, and plastics. A specific application is in structural insulated panels (SIPs) which involve bonding a foam core to solid wood and OSB or other panel products [297, 298].

Future

Their ease of use, the ability to drastically change their properties through formulation changes, and their good bonding ability to wood and other materials make polyurethanes favorable as wood adhesives. There are some challenges in the more demanding structural applications, but this has been an issue with many adhesives. Even with the ability to make PURs from different monomers and to control the ratios of hard and soft structures, there are still concerns about moisture delamination and heat sensitivity for structural products in tall wooden buildings, like those using cross-laminated timber [296, 299].

As in number of other fields, researchers are developing bio-based polyurethanes for a variety of applications, including adhesives [300, 301], specifically wood adhesives [241, 302]. Like most cases with formulated products, it is difficult to know what technologies are being used commercially unless the adhesive supplier indicates it.

Emulsion Polymer Isocyanates

Emulsion polymer isocyanates (EPI) or aqueous polymer isocyanates (API) are two-component adhesives that are newer to the wood products industry than most other adhesives [303, 304]. The first API adhesives were developed in Japan in the early 1970s and this adhesive type has been extensively used in Japan since then. These adhesives have become popular elsewhere since then due to licensing of the technology to other companies and referred to as EPI. Like the PURs, there is a wide formulation latitude, not only in the components used, but in the ratio of the components. A distinct feature of the EPIs is that they can set in minutes to an hour, like the epoxies, without added heat.

Chemistry of Adhesive Formulation

As the name indicates, an EPI has two main components, a polymer emulsion and an isocyanate emulsion, that are mixed just prior to application (Fig. 14.26). This makes it a two-component adhesive, like RF, PRF, epoxy, and 2C PUR. This technology has been considerably advanced since the original development of a PVAl emulsion and an emulsified isocyanate EPI adhesive, used in specialty applications [303, 304]. PVAl is made from PVAc by hydrolysis (partial or completely), so the PVAl can come in different types due to the degree of hydrolysis and polymer

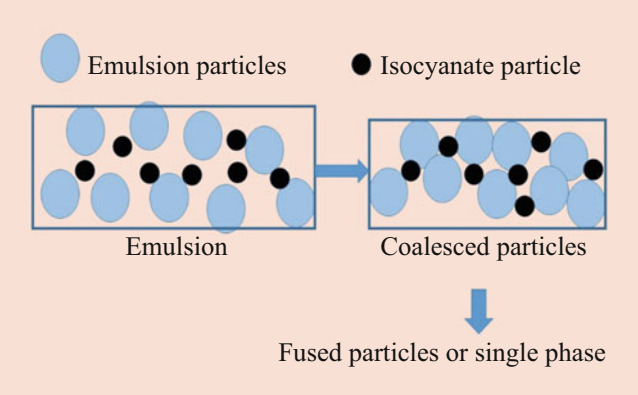

Fig. 14.26 EPI cure showing the coalescence of the two phases, but the final structure is still unclear

molecular weight. In addition, the amount of PVAl added to the vinyl acetate for emulsification and as a protective colloid for PVAc synthesis is used to control particle size [276, 277]. These variables determine the emulsification versus solubility ratio of the PVAl. The PVAl has many hydroxyl groups available to react with the isocyanate to form polyurethane linkages.

The emulsification of the isocyanate protects it from reacting too rapidly with water instead of the emulsified polymer. Emphasis has been placed on the type of emulsified polymer used in the formulation. Further developments using different types and amounts of polymer emulsions, including PVAl, ethyl(vinyl acetate) polymer (EVAc), styrene butadiene rubber (SBR) or acrylic-styrene emulsion, and combinations of these, have led to adhesives systems with improved versatility and performance [303, 305].

Having PVAl as the main adhesive makes linkages throughout the cured polymer much stronger than just bonding a PVAl protective colloid around a PVAc core. The PVAl has multiple roles in the EPI adhesive formulation besides taking part in cross-linking reactions with the isocyanate during curing; PVAl takes a major part in controlling the viscosity/rheology of the adhesive and preventing sedimentation of added fillers [303]. While PVAl is the most commonly used thickener, other reactive hydroxyl functional polymers, including hydroxyethyl cellulose and starch, are also used. However, controlling the number of hydroxyls in the latex (aqueous polymer emulsion) leads to a more uniform cross-linking in the latex film [306].

Although any di- or polyisocyanate can be used as a cross-linker in an EPI adhesive, the three main factors that are important for the choice of isocyanate for an adhesive are cost, volatility, and reactivity of the isocyanate [303–305]. While toluene diisocyanate (TDI), MDI, and pMDI are common, a variety of other diisocyanates and triisocyanates have been used [303, 306]. The isocyanates added to the emulsion polymer can react too quickly with the water; thus, there has been an emphasis on aqueous emulsified isocyanate where the pMDI is modified with nonionic surfactants to facilitate the dispersion of the pMDI into the adhesive [307]. Additionally, isocyanates can be protected from reaction with water by reacting the NCO groups with mono hydroxyl- or amino-compounds. Primarily solid TDI dimer is used for this application and the NCO groups on the surface of the solid isocyanate particles are blocked [303, 306, 308]. A MDI prepolymer formed by reacting MDI with a polyol to form urethane linkages can be used as a cross-linker for EPI adhesives [303, 309].

Fillers are used in EPI formulations for reducing the cost of the adhesive systems, increasing the adhesive solids content, improving the gap filling properties, and increasing heat resistance of the cured adhesive. Although calcium carbonate is the most commonly used filler, others such as wood fibers, shell flours, clays, silica, and talc have been used [303, 306].

Raw-Materials Source and Cost

PVAl is produced by partial or complete hydrolysis of PVAc. PVAl grades with different molecular weights and differing degrees of hydrolysis are commercially available (see Sect. 14.2.2.2 Polyvinyl Acetate in this handbook for information on PVAc synthesis). Production and application of the various emulsion polymers generally in use have been described in literature [310–312].

The preparation of MDI and pMDI are covered in the pMDI Sect. 14.2.2.1 Diisocyanate Adhesives of this handbook. The TDI is produced by a similar process of dinitration of toluene, followed by hydrogenation of the nitro groups, and then reacting them with phosgene to produce the diisocyanate and hydrochloric acid.

Chemistry of Cure with Conditions and Interaction with Wood

The advantages of using EPI adhesives are fast setting speed, cold curing, light-colored glueline, low creep of the glueline, and high moisture resistance of the bonded assembly. Depending on the formulation, EPI adhesives can be cured at room temperature and even some which cure at temperatures as low as 5 °C are available [303]. EPI adhesives can also be cured by heat or exposure to radio-frequency wavelengths. The complex morphology of the bonded EPI adhesives depends on water loss to the wood, film formation of the emulsion, and chemical curing reactions of the highly reactive isocyanate with water, hydroxy-, amino-, and carboxy-

groups on the polymer emulsion [303, 305, 308]. The large number of competing reactions between components of different and varying concentrations makes it difficult to predict the extent of different reactions occurring in an EPI adhesive mixture during curing.

To make the EPIs suitable for bonding in different applications, the adhesive manufacturer has considerable formulation latitude, which makes it difficult to be specific on the curing process [305]. The initial adhesive film formation may take from minutes up to one hour, depending on factors including temperature, emulsion type(s), solids content, spread rate, and wood species and MC. However, being a two-component adhesive, it is important to have good mixing and limit any precure (gelling) that can limit good adhesive spread.

Morphology and Other Properties of Adhesive

The bonded assembly will have very good mechanical properties if the coalescence of the emulsion particles and contact with the wood are optimal [303, 305]. For example, if the pot lifetime is exceeded and the isocyanate reaction proceeds too far before bond formation, poor wood contact is likely and adequate coalescence will not be possible leading to a more rubbery final consistency [305]. Poor emulsification of the nonpolar pMDI grades into the polar waterborne adhesive component results in partial phase separation during drying/curing, as well as in nonuniform crosslinking in the glueline [303]. Hence, a good balance between the mixing and bonding processes is essential.

These adhesives generally set quicker than the other isocyanates (pMDI and urethanes). Additionally, because these are aqueous emulsions, the loss of the water into the substrate is important to the final adhesive properties in that slow water loss and fast curing can lead to an adhesive with a lot of voids. Because the EPIs can be formulated with a wide variety of emulsions, it is hard to discuss the morphology in detail. However, it is known that the isocyanate provides the cross-link between the emulsion particles, see Fig. 14.26.

Durability in Moisture, Heat, and Decay

Specific EPI formulations provide very durable bonded wood products. EPI adhesives were first approved in Japan as a supplement to PRF adhesives for production of small and medium glulam beams used as load-bearing posts for indoor use [303]. They have also passed North American standards for structural adhesives, including D-2559 [313]. The final bonded product may initially have decent strength, but additional time is needed to develop final creep, heat, and moisture resistance.

Utility in Wood Bonding

The water-based emulsion adhesives with isocyanate as cross-linker are used in many parts of the world for production of different types of wood-based products such as: solid wood panels of different types, parquet, window frames, furniture parts, plywood, finger joints, and load-bearing constructions like glulam beams and I-beams [303]. Few adhesives can be tailored for such a wide variety of wood-bonding applications and providing such good durability, but the rapid set time limits its application the type of products that can be made from these adhesives.

Future

EPI chemistry allows for a wide variety of formulations to meet a wide spectrum of uses in providing a rapid set ability, ease of application, some gap filling ability, and good moisture and heat resistance. The adhesive manufacturer determines the formulation for each application because there will always to be trade-offs in application and performance properties for a specific formulation. The price is very dependent on the formulation, but in general, EPIs tend to be higher priced for a wood adhesive.

Proteins

Proteins were the main wood adhesives for centuries, but the origin of this technology is not clear since they were likely used as adhesives before recorded history. Early hieroglyphics show what looks like a hot adhesive bonding wood veneer to furniture. This was probably a collagen adhesive, which means that they knew how to cook collagen (hides and bones) with caustic or acid to make what is termed an animal adhesive [314]. Blood, milk, and egg proteins were used for adhesives or binders in paint. No adhesive formulations had been recorded, because keeping this formulation information secret was important for the formulator through the Middle Ages, Renaissance, and early industrial period. Gradually, information was made public on the hydrolysis of collagen from farm animals and fish, preparation of casein from milk, and use of blood and soy flour as the most common adhesive sources [315]. The following discussion is focused mainly on soy given its wide availability, low cost, and high protein content.

Chemistry of Adhesive Formulation

A protein molecule is a singular chain that usually forms a specific globular structure (native protein conformation) in their aqueous environments based on their sequence as they are synthesized. This structure does not apply to collagen proteins that are helical in shape and to other structural proteins. The globular proteins have both hydrophobic and

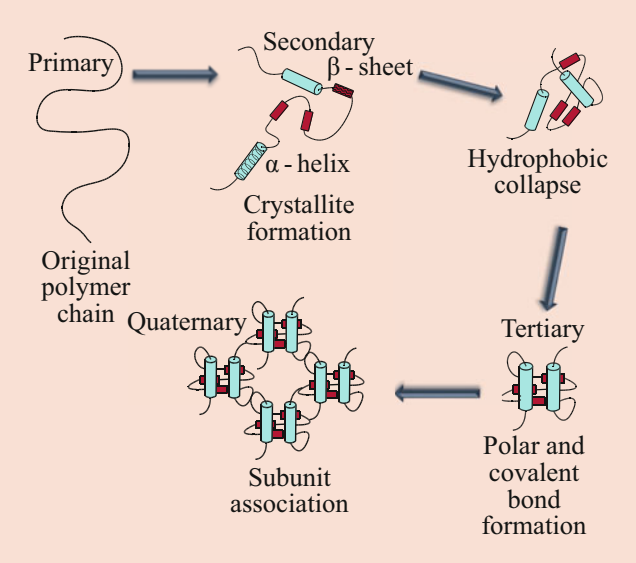

Fig. 14.27 Schematic of protein formation upon synthesis: the protein does not exist in a linear state of the primary structure, but forms crystallites and collapses during synthesis

hydrophilic patches on the surface as well as hydrophilic and hydrophobic domains inside the globular structure that are stabilized by self-association and absorbed/adsorbed water even in the solid state. Figure 14.27 shows that the protein chain develops its three-dimensional structure by forming α-helices and β-sheets along with hydrophobic collapse. These individual globular proteins enhance their stability by forming more stable aggregates with other proteins. For proteins, two measurement scales are used: the first is the kilodalton (kDa), which is used for individual protein chains, where a kDa has a molecular weight of 1000 grams per mole. The second is based upon the ability to separate protein agglomerates by size, where the Svedberg unit (S) offers a measure of a particle's size based on its sedimentation rate. It is these native aggregates, such as 11S (glycinin) and 7S (conglycinin) in soy, that the literature refers to as the protein adhesive [316–320]. The 11S is a well-defined structure of 12 protein chains of about 300–380 kDa arranged as two stacked hexagons, and the 7S is generally a trimer that is 170–200 kDa of different subunit arrangements [317].

Proteins are seldom pure in their natural sources and need to be separated from other bio-based materials. The most common and lowest-cost proteins are mostly from oilseeds, which are first processed to remove the higher value oil via an extraction process. The remaining meal is often used as animal food because it is a low-cost source of protein (about 45% protein), but it can also be ground into a flour for other uses. Although these oilseed proteins can have higher protein contents by conversion to so-called concentrate and isolate, the loss of material and the processing cost make them too expensive to use as wood adhesives, thus these products are mainly used in food applications. The soy concentrate (about 70% protein) has the soluble carbohydrates removed by extraction, while the isolate (about 95% protein) involves several separation steps to have both the insoluble and soluble carbohydrates removed [321].

Of the oilseed flours, soy flour is the best protein source based on availability, protein content,` and cost. However, soy needs to have a co-reactant for it to have good water resistance [315, 316]. One approach is to use it with phenolics, because both phenolics and soy flour are better adhesives under high pH conditions and provided good results for OSB production [311, 322]. Another effective way to produce an economical and commercially viable interior adhesive from soy is the addition of polyamidoamine-epichlorohydrin resin (PAE) with low epichlorohydrin residuals as a no-added formaldehyde (NAF) adhesive [323–325]. Other routes have been examined, but only a magnesium oxide-soy flour product seems to be used commercially at this point [326].

The soy-PAE adhesives are made by dispersing the soy in aqueous PAE co-reactant and additional water, adjusting the pH between 7 and 9 depending on the formulation and using the adhesive the day of manufacture.

Raw-Materials Source and Cost

Oilseeds are processed first by drying, cracking, and dehulling, and finally by pressing or extracting with organic solvents to remove the oil (fats) and leaving a flour after desolventization and milling [321]. This defatted flour is used "as is" for adhesive manufacturing. After removing the more valuable oil, some soy is used to make higher purity proteins that are used in food applications, but most of the remainder is used for animal feed after heat treating to make the meal more digestible. Other oilseeds that have been examined include rapeseed/canola, cottonseed, and lupine [327].

PAE co-reactant is made by first reacting a polyamine (e.g., diethylenetriamine) with a dibasic acid (e.g., adipic acid), then reacting this polyamidoamine with epichlorohydrin and caustic [328, 329]. These PAE products are available as aqueous solutions, generally at 20–30% solids. The main use of PAE is an additive that gives paper towels strength when wet by reacting with the carboxylic acid groups in the cellulosics to hold the cellulose fibers together under wet conditions [329].

Chemistry of Cure with Conditions and Interaction with Wood

The soy-PAE adhesive is stable in viscosity at ambient temperature for hours to a day depending on the formulation,

especially under more neutral conditions. This is feasible because many plywood plants have the equipment for making up simple adhesive formulations like adding fillers and hardeners to UF or soy-PAE. For plywood, the adhesive is applied to both sides of the cross-ply(s), often using a double roll coater. Bonding includes stacking the plywood of a normal ply, followed by a cross-ply with both sides coated and then a normal, etc., followed by cold pressing to let the adhesive transfer to the adjacent veneers and flow into the wood, and finally heat curing in a press to a glueline temperature of about 120 °C. After setting, the bonded assembly is ready for shipping. The initial bond is not as hard as a UF out of the hot press, since it takes about a day for the soy to lose enough moisture to completely set to yield a hard adhesive.

Morphology and Other Properties of Adhesive
The soy in water is colloidal in nature so the product is formed by the coalescence of the particles, which provides good dry strength. Without a cross-linker, the product in many ways is similar to uncross-linked PVAc in water sensitivity. The co-reactant helps tie these colloidal particles together. The wet strength of the coalesced particles increases with increasing bonding temperatures without or with a co-reactant [330].

Durability in Moisture, Heat, and Decay
Although the soy-PAE adhesive passes plywood soak tests, it has not been demonstrated to have high enough water resistance to yield good wood failure. The soy interior products have shown good stability under normal use conditions. Unlike the coalesced adhesives PVAc and PVAx, the soy products have excellent heat resistance [331]. In fact, heat strengthens the bond, which is why casein (from milk) and casein-soy are used in fire-resistant wood panel doors. In addition, casein protein adhesives have shown to last in structural products for decades as long as they did not have high moisture exposure [332].

Utility in Wood Bonding
Soy flour with a PAE co-reactant is widely used in commercial interior plywood in the United States as a NAF (no added formaldehyde) adhesive to address those cases were the customer does not want to use a formaldehyde-containing adhesive for interior products. While the main market has been for plywood products, it has found some utility in other wood products, including engineered wood flooring [333]. Most interior plywood plants in the United States make up the adhesive formulation from preformed adhesives or raw materials to adjust the final formulation for plant conditions and type of wood being bonded.

The utility of soy-PF, especially the neutralized dispersion, has not been fully explored commercially [211, 322]. With a neutral pH, the product is more viscosity- and dispersion-stable than a normal resole PF, does not give a caustic burn to the wood product, and is tannish in color compared to the dark brown-to-black of a typical PF adhesive. Although a commercial OSB trial was successful, the process has not been commercialized.

Future
The oilseed protein adhesives will probably continue for interior laminated products where the customer wants a NAF product. However, a greater understanding of proteins and how to develop a stronger cross-linked product when exposed to water is needed to move outside their currently limited market areas.

14.2.2 Fundamentals of Wood Bonding

The immense number of wood-bonding applications increases the need for both many different types of adhesives and a number of formulation variations within each of these types [334]. Most wood adhesives are waterborne, making the process of curing very complex due to the simultaneous penetration of the adhesive into the wood, loss of water through absorption by the wood, and a variety of chemical reactions taking place leading to decreased adhesive mobility. In addition, with heat-cured adhesives, the temperature varies in different parts of the bonded assembly. The wood type and surface preparation also influence all these variables.

Wood Species and Substrates

The performance of an adhesive joint or a bonded product depends on various factors [115]. The adhesive and application factors are covered in Dunky's section in ▶ Chap. 24 of this handbook, but many aspects originate from the basic properties and preparation of the wood. Wood is an inhomogeneous, hierarchically organized porous substrate, which is hygroscopic, has low thermal conductivity, and can be classified as a brittle to ductile substrate depending upon the moisture content [335]. Wood is inherently anisotropic, influencing its mechanical properties and other physical properties, such as directional swelling and shrinkage behavior, thermal conductivity, and permeability. Although the basic chemical composition has been determined for most wood species [335, 336], the chemical composition of the bonding surface is less well understood. A freshly prepared surface has more exposed structural polymers, but extractives will migrate to the surface over short periods of time, and the chemical composition of the lumen walls has not been well characterized. Other factors include the pH and buffering capacity of wood [337], which can alter the cure of amino and phenolic resins that are pH sensitive, especially near the interface [338–341].

Although the wood surface chemistry and structure are most important, practically, we are limited to the analysis of the bulk wood for research studies and general knowledge of the wood species for commercial production. While many properties of wood may be important to the performance of the bonded assembly, the discussion below concentrates on the key factors that influence the ability of the wood to bond sufficiently well to meet product performance requirements.

The wood cellular structure [342] is influenced by the section of the tree (e.g., pith, juvenile wood, heartwood, or sapwood), reaction wood, and growth-ring factors (e.g., earlywood vs. latewood, abrupt vs. gradual transition). In addition, species greatly differ in density, acidity, extractive type, ratio of heartwood-to-sapwood, and softwoods vary in density differences between earlywood and latewood. While hardwoods vary in being diffuse porous or ring porous, and in many other ways [343], all of these differences can play a role in bond formation and durability.

Hygroscopic Behavior

Early descriptions of the influence of moisture on bonding ability indicated an influence of wood MCs on the gluing process [344]. The MC at the time of bonding is not always the same as the MC at the time of use or testing. While tests are typically carried out at 12% MC for most adhesives today, dramatic losses in bond strength for casein bonds were determined in 1952 to start between 13% and 20% MC [344]. MC in the bulk wood or on the surface is an important parameter that needs to be well controlled [343]. The MC of wood is dependent on the humidity and temperature and whether the wood is increasing or decreasing in moisture content. The surface MC can vary considerably on a veneer due to uneven MC of the starting green wood. The surface MC can greatly alter the bonding in that high MC makes bonding with polycondensation adhesives (e.g., UF and PF which release water) more difficult, while low MC hurts the cure of isocyanates, which consume water. In addition, the swelling and shrinking of the substrate can introduce significant stresses and weaken the bond strength during use. There is extensive literature on the MC influence on bond formation and bond durability and its effect on product design, especially for plywood [334, 345, 346].

As an additional aspect, MC will alter mechanical properties of wood [347]. For example, the MC and the temperature have to be considered for selecting an effective pressure during pressing. Increasing humidity, and also increasing temperature, will directly influence the strength of the wood substrate, at that high MC, the wood water dilutes waterborne adhesives and can cause over-penetration. In addition, excessive pressure should be avoided since too much pressure may lead to a mechanically induced in situ weak boundary layer, which only some adhesives can repair during bonding.

Extractives

Even though extractives are minor components of domestic wood species and a major components for some tropical wood species [348], they can make it difficult to form strong and durable bonds. The main problem is that the extractives create a chemically weak boundary layer (CWBL) by inhibiting the adhesive from developing bonds to the structural polymers in the wood cell walls [132, 349]. The type of extractive that can cause a problem is species dependent. Some tropical hardwoods, like teak, can be very oily and can be improved by solvent wiping of the surface before bonding. Terpenes are common extractives in wood, especially in softwoods. Extractives are mostly nonpolar, so once they migrate to the surface after machining, they will reduce surface tension, but they tend not to develop a high concentration at the surface because they can evaporate during any drying operation. Southern yellow pine can have low polarity pitch smeared across the surface by exposing the resin canals in preparing the bonding surface, which is not easily removed and can cause problems in developing strong adhesion to the wood.

While some extractives make it difficult for the adhesive to reach the wood surface, other extractives may give the wood a mechanically weak boundary layer (MWBL). An adhesive can bond to low-molecular-weight carbohydrates that are extractable and may come lose during water durability tests. This has been observed in synthetic polymers where low-molecular-weight oligomers migrated to the surface and provided a MWBL [110, 350].

Extractives not only can interfere with the adhesion to the wood polymers but also can interfere with the cure of the adhesive [340, 351–353]. The alteration of cure rates mainly influences the in situ cured adhesives, especially the formaldehyde-based ones that are pH sensitive. Different species of wood have varied pH values and buffering capacities. Some of the curing reactions are also sensitive to metal ions, which can be leached from the wood by the adhesive [338].

The studies of extractive effects have usually been done when the adhesive is used to laminate layers of wood together, but a lot of adhesives are used to bond particulate composites. Particleboard and fiberboard should be more sensitive to extractives than laminates due to the large exposed surface areas, but it is not known if there are any specific studies on this. However, the waxy surface of straw has been a major of obstacle for non-wood products, such as strawboard, and has limited the adhesive use to pMDI.

Some species present their own specific problems, for example, larch with its unusually high content of arabinogalactan, which is a water-soluble highly branched polysaccharide that has been proposed to interfere with bonding [354–357].

Mechanical Properties and Pressure

The mechanical properties of wood have a very important effect on bond performance in both bond formation and bond testing [334]. In bond formation, the higher density wood are more difficult to bond due to poor adhesive penetration and less mechanical interlock [345]. While adhesives can form good mechanical interlock with softwood earlywood cells because of their larger accessible lumens, they have more difficulty penetrating the thicker walled and stronger latewood cells. Wood like southern yellow pine is often more difficult to bond because of the large density differences between earlywood and latewood. For hardwoods, adhesives have more difficulty penetrating the small fiber cells, but readily go into the large vessel elements, which consume a lot of adhesive without an equal increase in bond strength. Due to the anisotropic nature of wood, the penetration is mainly in the longitudinal direction, though also it occurs to some extent in the radial and tangential directions. The curing of the adhesive is usually isotropic, but near the surface it likely follows more the orientation of the wood cells due to the topography of the wood surface.

The optimal bonding pressure is very dependent on the mechanical properties of the wood in that higher pressure can aid in adhesive penetration into the wood, but too much pressure can cause glueline starvation by over-penetration and crushed wood cells. Denser wood species generally require higher bonding pressure to obtain adequate adhesive penetration, while less dense wood requires lower pressure to avoid starvation of the glueline and crushing of the cells creating a weaker wood surface [115]. A high percentage of wood failure despite low bond strength, especially under wet conditions, is usually an indication of a damaged wood surface [345]. The correct pressure is dependent on wood species, moisture, temperature, and adhesive properties, which can be determined only by experience and analysis of the product. For particulate composite panels, the situation is even more complex in that density, temperature, moisture, and pressure are nonuniform from the top-side through to the bottom-side of the panel [358, 359].

Low Thermal Conductivity

One of the advantageous properties of wood is its poor heat transfer making it a good insulator for building exterior walls. However, this insulating aspect also makes it difficult to bond with adhesives that need heat for curing, especially for thick products [344]. Induction of heat by contact was studied by Bryante and others in the 1940s, radio-frequency methods also had already been known at that time. Instructions for calculation of press time for plywood-type panels as the time at a particular temperature to set the glue itself plus the time required to heat up the glueline were already known. For heat penetration in solid wood or plywood, one minute per millimeter of wood thickness between platen and the deepest glueline have been proposed as a simplified rule. The rule itself is an oversimplification as temperature penetration for thin substrates is known to be faster than for thick ones [344]. When the platen temperature is above the boiling point of water, the temperature penetration rates become more complicated. The temperature itself is limited by the boiling point of water for thick substrates. In a general discussion, Habenicht mentioned that low thermal conductivity is a considerable limitation in using temperature curing adhesives when producing boards where sufficient heating up is not possible by steam convection [360].

The heat movement is different for wood-based panels using particulate or fibrous materials. The moisture movement from the surface also moves heat to the interior. Due to the presence of water and the resulting vapor pressure, curing temperatures in the core of panels (e.g., in particleboard or fiberboard) is typically limited to approximately 110–120 °C, even with high press temperatures of more than 200 °C. Too much heating on the surface can cause scorching and too much heat in the interior can cause higher steam pressures resulting in blows (delamination) in the core [359]. The temperature limit can be overcome using extremely long hot pressing times and absolutely dry wood, but this is not a real option for the industrial praxis.

Surface Preparation

Surface preparation is as big of factor along with adhesive resin, wood type, and bonding conditions [115, 344, 345]. The key aspects of having a sound wood surface free of defects, that are flat with a low grain angle in the wood, and being planed (best) or lightly pressure sanded to remove contaminants are not surprising. A MWBL or surface inactivation, as described in the following paragraph in more detail, makes having strong bonds more difficult. In addition, differences in adhesive receptivity by variation in earlywood versus latewood, and mature versus juvenile versus heartwood all make a difference. Although these items can be better controlled in laboratory studies, commercially, unevenness in MC, earlywood/latewood ratio, grain angle, and extractives are common.

Surface Inactivation

The free surface energy of a wood surface is the highest when freshly prepared, then decreases over time. As the surface energy is reduced, wetting of the wood with most adhesives becomes more difficult and results in decreased adhesion of the adhesive to the wood surface, reducing bond performance. This reduction in surface energy is often referred to as surface inactivation, surface contamination, or ageing of a wood surface [361]. This effect itself was reported many decades ago by de Bruyne in 1937 [344], who observed the

non-gluing of spruce plywood in aircraft manufacturing that was called "casehardening of wood." The causes of casehardening were attributed to chemical changes of the wood surfaces as a result of intense heating and drying in the manufacture of plywood and, hence, a loss of polar groups on the wood surfaces.

Surface inactivation is a well investigated and documented effect as summarized by Piao et al. [362] including its influence on bond strength. The causes of this effect have been studied, but specific mechanisms are still being debated. In addition to the earlier proposed loss in polar groups, various further explanations have been reported, including migration of wood extractives to the surface, also described as self-contamination [363]. Dirt, dust, and grease contaminating the surface, oxidation processes occurring on the surface [361], and dehydration of wood hydroxyl groups have been also reported [115, 362].

Extractives are frequently mentioned as migrating to wood surfaces to explain the drop in surface energy with time [364]. Gardner et al. [349] specified the migration of low-molecular-weight extractives to the wood surface and the oxidation of those thereafter. Wood dried in a nitrogen environment proved to be less inactivated than wood dried in air, based on the values of bond strength and wood failure; this is seen as a proof for oxidation occurring during drying. Others [343] supported the idea of extractive migration where no loss in surface energy of extracted wood could be observed after ageing of different surfaces for a period of 1 week, whereas the surface energy of non-extracted wood clearly deteriorated.

According to Piao et al. [362], only "non-wettable" extractives appear to be commonly accepted as the major cause for deterioration of the surface with time. He assumed that at room temperature, it is almost impossible for solid polar organic extractives to "migrate" to freshly cut surfaces. Therefore, both water and to a lesser extent low-molecular-weight VOCs are likely responsible for contamination or the ageing phenomena of freshly cut wood.

After surface generation, freshly exposed molecules are rather reactive due to remaining valence electrons [365]. In the reduction of the high energy, the surfaces tend to be covered by other molecules, like dust and oils, or react chemically with gases, such as organics, oxygen, or other oxidants.

Time is a significant variable affecting wood surface energy, wettability (Sect. 14.2.3 Wetting of this chapter), and consequently adhesion [366]. Total surface energy diminishes with surface age (Fig. 14.28a and b). Surface acid components increase and the corresponding base components decrease based on wetting experiments. It is believed that oxidation of extractives is responsible for the increase in acidity. After ageing, a reduced O/C (oxygen/carbon) ratio was found based on XPS (X-ray photoelectron spectroscopy)

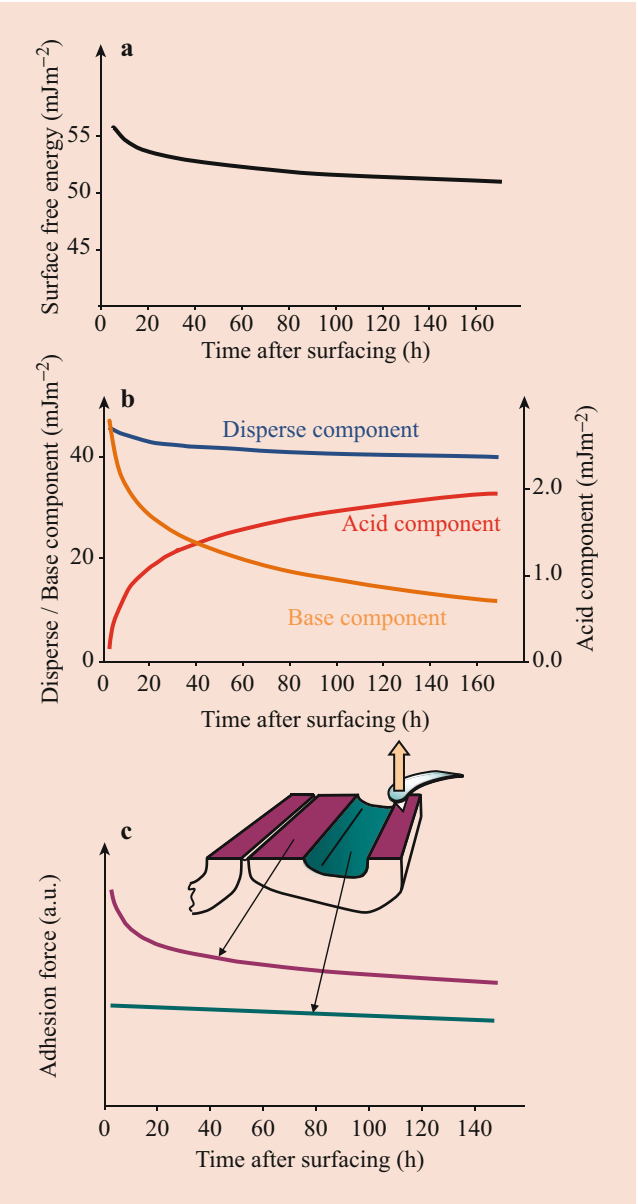

Fig. 14.28 Time dependence of surface free energy (**a**), and its disperse, acid and base components (**b**) determined by contact angle measurements of sanded spruce wood (redrawn from Ref. [366]); (**c**) time dependence of adhesion force (related to polarity) of lumen and cell wall surfaces determined by atomic force microscopy. (Redrawn from Ref. [367])

experiments indicating a decrease of polar components. It is widely agreed that aged surfaces are more hydrophobic [121, 363] and their wettability by water is reduced.

Using investigations on the microscale by atomic force microscopy-based adhesion force measurements on longitudinally microtomed spruce wood surfaces, Frybort et al. [367] attribute the local origin of ageing in large part to secondary cell wall S2 surfaces, whereas lumen surfaces did not show distinct ageing behavior (Fig. 14.28c).

Correspondingly, S2 surfaces showed high adhesion forces and thus polarity immediately after surface generation by microtoming, whereas lumen surfaces were significantly lower in polarity. After ageing, the level of polarity of the two surface types approximated each other. This difference in surface condition was shown to affect local adhesion of adhesives to the different cell wall types in two opposite directions for different adhesive types [368]. A more polar, water-based UF resin showed higher adhesion towards freshly cut S2 cell walls, whereas a less polar polyurethane adhesive showed higher adhesion towards less polar lumen surfaces.

Different from surface inactivation at ambient conditions, the effect of overdrying from high temperature drying (excessive time and/or heat) on bonding has been a major issue, especially in plywood production. Christiansen [135, 369] differentiated in his extensive reviews between physical and chemical responses of wood to excessive drying. In addition to the aforementioned main factor of extractive-related non-wetting, Christiansen discussed reorientation of molecules at the surface, and irreversible closure of larger micropores in cell walls. Reduction of wood surface strength, oxidation, pyrolysis of wood bonding sites, and chemical interference with resin cure or bonding, as well as, elimination of surface hydroxyl bonding sites by ether formation [135] were also identified. Because multiple time-dependent processes occur during high temperature drying, it is not easy to attribute inactivation to single cause, as duration, temperature, and wood species have to be considered as factors. Sernek et al. [370] investigated the effect of high temperature drying and found distinct chemical surface modifications indicating higher amounts of nonpolar groups when dried at high temperature (>160 °C), as well as its impact on wettability and bond performance. In the example of a 1 h thermal treatment performed at different temperatures between 60 °C and 200 °C, a gradual increase in water contact angle from 65° to 145° between lowest and highest temperature was found [371].

It can be concluded that surface inactivation continues to be an issue important for wood adhesive bonding. For structural solid timber bonds, a clean and freshly prepared surface by planing or lightly sanding to avoid crushing surface cells is critical to obtain sufficient bond strength and durability. Generating fresh surfaces are obligatory and required by some product standards for structural materials using solid wood lamellas such as glue laminated timber, cross-laminated timber, and the like. Depending on wood species, adhesive joints have to be bonded within 6 h for extractive rich for difficult to bond species, or within 24 h for regular species after surface generation [372]. From practical experience, the shorter the time from planing to bonding, the better.

As a result of the chronological order of processing veneer- and particulate-based materials (e.g., for plywood, laminated veneer lumber, parallel strand lumber, OSB, particleboards, and MDF boards), the materials are usually with thermally dried, comparably old, and consequently inactivated surfaces. The substrates are generated first by some kind of disintegration technology in the wet or green state. Typically this process step is followed by some kind of drying treatment at high temperature, typically before the adhesive is applied and the material is bonded. Usually no process step is performed to improve surface conditions after the drying step (e.g., sanding); so the surfaces undergoing these process steps are significantly different from those described for the solid timber joints. It is therefore expected that local adhesion and the resulting bond strength between wood and adhesive is often significantly below that for solid wood joints. This is probably less true for the non-water dispersed isocyanates, especially pMDI.

Adhesive Interaction with Wood and Other Substrates

Wood surfaces are extremely nonuniform with heartwood versus sapwood, mature wood versus juvenile wood, earlywood versus latewood, and the various types of reaction wood. Additional factors are the orientation of the wood surface to the tangential, radial, and longitudinal axes, whether the surface has been prepared by sawing, planing, sanding or fibrillation, ageing, method of drying, MC, etc. All of these influence the adhesive interaction of wood and the bond strength [115]. Consequentially, it is difficult to describe even the interaction of a single adhesive with wood and how this relates to overall bond strength. Given the multitude of adhesive formulations, it is difficult to develop an all-encompassing model; however, years of experience along with some fundamental studies have given adhesive manufacturers and users good empirical understanding of how to make good bonds. With the high cost of adhesives, the wood products manufacturer wants to reduce the amount of adhesive by having sufficient but not excessive penetration or glueline thickness. For bonding and bond failure, it is important to use the best and most convenient test method to understand the adhesive wood interaction [373]. There are a number of reviews and books that cover the adhesive-wood interactions [127, 138, 140, 143, 212, 309, 349, 354, 363, 373–380].

Wetting

For adequate adhesion, an adhesive needs to have intimate atomic or molecular contact with the substrate across a common interface. Physical adhesion must first take place before any other bonding processes, such as chemical reaction can occur, see Sect. 14.2 of this handbook. The physical adhesion depends on the strength of intermolecular force interaction on

the area of contact and on the distance separating the atoms from the top layer of each surface [381]. Considering that at some stage in the process the adhesive will flow, wetting refers to this intimate interaction between adhesive and substrate. Therefore the adhesive (and primer if one is employed) needs to be able to spread over the solid surface and needs to displace air and contaminants that may be present on the surface [382].

This physical or thermodynamic adhesion, adsorption, or wetting is described as one of the adhesion theories especially important for wood bonding [349] since it is a prerequisite for interfacial strength development. Its importance for joint strength is also evident for general adhesive applications when a joint is initially formed [382].

The term *wettability* [383] is defined as the ability of a liquid (adhesive) to spread on a specific solid surface. The extent to which a liquid wets the solid surface can be conveniently measured by contact angle techniques on flat adherend surfaces. When a liquid comes into contact with a solid surface, it remains either as a drop or spreads over the surface until a balance between adhesive and liquid cohesive forces is reached, given that no penetration into the substrate occurs. The contact angle θ is the angle between the tangent to a liquid drop at the solid-liquid-air contact point and the solid surface under the liquid. Thereby, a low (theoretically $\theta = 0°$) contact angle indicates a perfect wetting of the solid, whereas a high contact angle of maximum $\theta = 180°$ indicates poor or no wetting. At a contact angle of less than 90°, sufficient intimate contact for spreading is assumed. This condition is only fulfilled if the surface free energy of the solid (wood) is equal to or higher than the surface tension of the liquid [384].

The relationship of the balance of the energy components as vectors was already described in 1805 by Young using following equation:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV}\cos\theta$$

where γ_{SV} is the interfacial tension at the solid-vapor boundary (surface free energy), γ_{SL} is the interfacial tension at the solid-liquid boundary (interfacial tension), and γ_{LV} is the surface tension of the liquid (liquid-vapor boundary).

Wetting, also referred to as physical adhesion [381], is regarded as a competing process of adhesion forces with cohesion forces within the liquid. Surface tension of a liquid and surface free energy of a solid represent these forces and are regarded as fundamental material properties. Forces involved in wetting include: (a) acid-base interactions, (b) hydrogen bonding, and (c) van der Waals forces (dipole-dipole and dispersion forces) [349]. In the extensive reviews about contact angles and wettability of wood [362] and cellulosic surfaces [385], the authors describe in detail the historical development up to the current state of the art on fundamentals related to wettability, including parameters such as critical surface tension, which is the highest value of surface tension of a hypothetical liquid that will still wet a given surface. The polar and dispersive terms, as well as, acid-base contributions add to free energy and estimation of work of adhesion ($W_{adhesion}$) is also described in detail. The work of adhesion is composed of the different interfacial tensions as follows:

$$W_{\text{adhesion}} = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}$$

Having the relationship from this equation, it is evident that interfacial tension γ_{SV} between the adhesive and the substrate is critical for adhesion and consequently joint strength as pointed out by Mittal [386]. While this equation is fundamentally correct, it only describes what happens at the interface under ideal conditions, the actual work of adhesion in nonideal conditions is much more complicated.

Practical experience over a long period has shown the importance of adhesive wetting for wood adhesion. The theoretical concept of wettability for wood bonding was systematically applied in the 1960s [387, 388]. Boundary conditions are required by Young's equation, where the substrate should be ideally smooth, homogeneous, and without any impurities and adsorbed gasses. Furthermore, the substrate should not be soluble in the liquid drop, and the liquid should not penetrate into the substrate and/or cause its swelling. In contrast, wood with its complex structure and chemical composition is extremely far from being an ideal substrate [389]. A range of factors influence contact angles of liquids on wood: surface roughness (machining, anatomy), chemical composition, extractives, ageing, surface contamination, MC, treatments (e.g., plasma treatments, wood modification, densification, and so on), and much more.

As these overlapping actions take place, it is not trivial to study and describe the wetting process of wood surfaces when the contact angle significantly changes with time. Wetting models, as proposed by Shi and Gardner [246], could be used to describe the adhesive wetting process for wood substrates including (1) the formation of a contact angle at the solid and adhesive interface, (2) spreading of the adhesive over a solid surface, and (3) adhesive penetration into the porous solid substrate.

The most common methods to determine surface energy and wettability of wood are sessile drop and Wilhelmy plate. These methods together with a range of others, such as inverse gas chromatography IGC, are reviewed in the context with their applicability and significance for testing wood surfaces in detail [349, 389]. In addition, the acid/base approach as shown by Gindl et al. [390] is most suitable for calculating surface free energy of wood.

Typical values for surface free energy of wood surfaces range from 35 to 70 mJ/m^2 [343, 362, 391, 392], thus

representing low energy surfaces only slightly above a wide range of common synthetic polymers. The main factors influencing surface energy and thus wettability of wood are described in detail elsewhere [362, 389] and can be related to the liquid (viscosity, temperature, etc.), the wood species and its structure (local proportion of earlywood and latewood, grain orientation, sapwood, heartwood, etc.), anatomical microstructure, physical properties of the wood (moisture, temperature [393], density, drying history, etc.), chemical properties of the wood (composition including the presence of extractives [394]), machining methods and resulting roughness, chemical and physical wood treatments (e.g., heat treated) [370, 395], fire retardants [396], preservatives, ageing [392], and the measuring technique. An area that has received less attention is the effect of the adhesive on altering the surface energy of the wood. The high pH of phenolics should extract some of the inherent chemicals from the wood and can alter the wood surface structure. Both of these can alter the wetting characteristics of wood.

Data on the surface tension of liquid adhesives are less frequently published. Shi and Gardner [246] report surface tension from advancing dynamic contact angle measurements for a PF to be 52 mJ/m^2, a somewhat higher surface energy compared to the pMDI (41 mJ/m^2) using the same method. Surprisingly, other PF and lignin containing adhesives were found to be around 40 mJ/m^2 [397]; thus, the adhesives may be in a similar range compared to wood surfaces [398, 399], but caution is needed in interpreting this data since the method can have a big influence on the measured values. The differences among contact angles are also related to the nature of the adhesives. As PF resins are regarded as more hydrophobic than UF resins because of the phenyl rings present in their structures, wettability will be different (polar/disperse contributions) [349]. When extractives and acid/base interactions play a significant role for the wood species, more careful analysis would have to be used to get meaningful information about wettability.

Penetration

Wood is a very unusual substrate in that the adhesive and solvents can penetrate into it [400]. Penetration describes all chemicals that move through the wood surface, but there are two types of penetration [127, 133].

The main pathway for all adhesives is the flow of the bulk adhesive across the surface and into lumens, which are controlled by the adhesive viscosity, surface tensions, time, pressure, and temperature. The capillary flow of the adhesive through exposed lumens is determined by the Washburn equation [401]. Of these variables, the one that is likely to change the most during bonding is adhesive viscosity, which increases as the water moves from the adhesive into the wood structure and the adhesive cures. This type of penetration increases mechanical interlock and the surface area for adhesion. However, it does not change the cell wall properties and is unlikely to repair cell wall damage [140, 164]. Pre-polymerized adhesives are basically confined to this method of interacting with wood.

Low-molecular-weight and polar adhesive components can infiltrate the cell wall [378]. A wide variety of methods have been developed to show the infiltration of such adhesive components in wood cell walls [373]. As previously discussed, cell wall modification is important to the performance of in situ polymerized adhesives and wood properties (see Sect. 14.2.2.1). In general, chemicals that enter into cell walls can swell these walls and make them less likely to swell further by absorbing water under wet conditions. The effect of cell wall modification has been extensively covered in the wood modification literature [402–404].

Modification

Although wood is a very important building material, there are two negative properties that have impeded their utility in this application. These negative properties are the dimensional change of wood with changes in exposure to moisture, and deterioration of wood by fungi, termites, ants, etc. Many methods have been examined for reducing the decay process of wood by modification [402, 403, 405–410]. However, many of the original methods were to treat with toxins (e.g., CCA-treated wood) or to reduce the wood water uptake (e.g., creosote).

Given the available excellent discussions on wood modification, we will not discuss details here but cover how the changes in the wood influences the ability to bond wood with adhesives. There are a number of individual studies on bonding modified wood, but the data is so limited and drawn from different processes with different adhesives and wood species that drawing any general conclusions is risky. An exception is the work done at the Forest Products Laboratory to study bonding of acetylated wood [380, 411]. A more recent study showed that bonding of acetylated wood is more difficult and more complex than just the reduced polarity of the wood surface [412]. Two main factors have to do with the reduced water absorption by the wood that not only influences the morphology of the adhesive curing, but also means that the wood retains much of its strength so that more force is placed upon the bondline after water exposure.

Reduced Swelling

The main modification for increased durability is to inhibit moisture uptake by providing a boundary layer (e.g., wax used in PB), or by altering the cell wall composition to decrease its hygroscopicity [362]. The latter is currently used for solid wood products and can be carried out in

many ways, with the most common being acetylated and heat-treated wood, both of which are commercial processes [402, 403, 407, 410].

The acetylation of wood involves treating dry wood with acetic anhydride to convert the hydroxyl groups to acetyl groups, which reduces the hydrogen bonding of wood and bulks up (swells) the cell walls [410, 413]. A main supposition was that the less-polar acetylated wood would be hard to bond with polar waterborne adhesives, but the polar PF, PRF, and RF waterborne adhesives gave strong wood bonds even when tested under wet conditions [380, 414]. Water soaking softens the adhesive, but not the acetylated wood, allowing high force to be applied to the bondline compared to unmodified wood bonds while the adhesive is weaker from the plasticization [412]. The high force by unplasticized acetylated wood on the plasticized adhesive is an important part of why acetylated wood is "harder to bond" than the unmodified wood which also becomes weaker when water soaked.

Wood can be heat treated to dehydrate some of the cellulosic polymers, which makes the wood less likely to adsorb water [402, 403]. Complicating the adhesive-bonding evaluation is that there are a number of different heat-treating conditions yielding in products with quite different bonding properties. While there are some individual studies on the bonding of specific heat-treated wood with specific adhesives, there are no systematic studies that we aware of relating the degree of heat treatment to the bonding ability with different types of adhesives.

Primers

It is not clear if wood primers are being used commercially in wood bonding processes. However, there have been a number of laboratory investigations showing the effectiveness of different primers. An early example was when an epoxy unexpectedly performed almost as well as PF adhesives in exterior exposure and in a very intense accelerated test of boil/dry cycles [167]. The explanation for the epoxy's very good performance was not explored in this paper, but another paper mentioned that it seemed that it was related to the use of polyethyleneamine primer, which made the epoxy perform better than all other adhesives except for the phenolics [252]. The most intensively studied primer has been hydroxymethylated resorcinol (HMR). Although the HMR has been shown to be effective with a number of adhesives besides epoxies and with a variety of wood species [142, 272, 415, 416], a specific mechanism for this bond durability improvement has remained elusive despite a number of theories [416].

Other wood primers have included a 2% aqueous solution of polyethylenimine [252, 417], melamine-formaldehyde [418], and dimethylformamide [142, 419]. Wood adhesive primers have not been examined as much as primers for wood coatings; thus, there is less insight for adhesive primers.

14.2.3 Adhesive Strength

Adhesives are used to hold wood pieces together or to bond wood to other materials. Adhesive performance in use is mainly a mechanical issue. Besides adhesive strength and location of failure, the performance of adhesive bonds in use is characterized by the viscoelastic behavior of both the adhesive and wood substrate, including their creep and heat resistance.

The classical definition of mechanical strength of a material is its ability to withstand a stress resulting from external forces. Ultimate strength is the maximum stress a material can tolerate and is typically calculated by the maximum external force applied, divided by the original cross section of the test specimen, e.g., by applying normal (tension, compression) or shear loads [420]. These measurements also reflect internal loads developed by adhesive volume reduction during curing, or stress caused by swelling of the wood under wet conditions. Besides ultimate strength, other strength levels are also defined, e.g., yield strength and fracture strength, describing the stress levels at which yielding or fracture occurs. Yielding is defined as the stress level of the first plastic (i.e., non-recoverable) material deformation.

For most homogeneous materials, the determination of strength values as well as other important mechanical properties of the material (e.g., elastic modulus, Poisson ratio) are relatively straightforward processes and result in reliable and reproducible material properties [360, 420], such as tensile strength, shear strength, Young's modulus, shear modulus, creep, and relaxation moduli. Due to the polymeric nature of most adhesives, such tests have to consider specific ambient and loading conditions (mainly temperature, load duration, etc.) that are finally used for the design of bonds and acceptable performance of the bonded product.

Even for non-wood applications [421], the amount of validated adhesive material properties, data (in a fully cured state, describing mechanical properties of in use conditions) published for adhesives that are suitable for design calculations, is extremely low relative to the wide range of adhesives that a design engineer may wish to consider.

However, cured adhesive polymer materials, without the presence of substrates, can be characterized according to typical "polymer" standards [422]. For most adhesives used for wood applications, such characterizations are extremely rare for various reasons as reviewed by Stoeckel et al. [423]. The chemical nature of a range of wood adhesives, and the polymers formed thereof, require the presence of the wood for appropriate curing and formation of solid, intact polymer

bondlines. In the absence of wood, very brittle amino-based adhesives (UF, etc.) decompose to powder and can rarely be characterized macro-mechanically. All polycondensation adhesives need to release water and tend to show a considerable offset in mechanical properties when cured without the presence of water absorbing wood substrates [424]. Other types of adhesives, such as isocyanate containing ones, typically require the presence of water in the wood or externally added water to undergo the required chemical cross-linking reaction (e.g., 1C PUR, pMDI), but this also creates carbon dioxide bubbles in the adhesive.

Because the performance of wood adhesives cannot be obtained separately from that in a bonded wood assembly, there seems to be no way of knowing characteristic mechanical properties such as strength or modulus of the adhesive itself. However, these mechanical properties were shown to influence the performance of adhesive joints [115]. Comparing the performance of PF and PVAc bonded joints, PVAc apparently performed better in terms of ultimate dry strength due to its ability for stress relaxation. This same adhesive failed in service under long-term load, with the latter load situation being perfectly suitable for a PF adhesive.

In the future, it may be possible to come up with wood-based applications where advanced computer-aided design and numeric modeling tools are state of the art for designing assemblies. The first step would be to design single wood adhesive joints that accurately predict the bonded product performance. This would bring wood products closer to other structural products, such as steel, iron, aluminum, and concrete. Literature and approaches for designing adhesive joints can be found in numerous textbooks [284, 425–427]. According to Brockmann et al. [384], modern finite element analysis methods allow a prediction of the stress distribution and deformations to be expected during service life in an adhesively bonded joint, provided that the relevant material parameters are available. Only then, it will be possible to exploit the full potential of adhesive bonds and the realization of economically optimized joints.

As very general design considerations, the following is recommended: avoiding peel forces, generating compressive stress rather than tensile stress, and avoiding stress concentrations in the bondline.

Adhesive Joint/Bond Strength

For wood adhesive bonds, joint strength is not a simple intrinsic adhesive property but is influenced by a range of interacting adhesive and adherend related factors, combined with the processing conditions of the bond and the geometric configuration of the joint, as well as the service conditions in use, as shown in Fig. 14.20. The influencing factors on bond performance are numerous and only a selection is included in the figure. A more detailed description of the factors affecting the properties of the individual bonds can be found in corresponding textbooks, reviews, and sections within this handbook, e.g., basic physical and mechanical properties of the adherend wood [335, 428, 429], adhesive properties [423, 430, 431], and the bonding process [115, 334, 360, 365] (Fig. 14.29).

In a cured bond, joint strength depends on adhesion properties of the adhesive to the substrate (interface), as well as the cohesion properties of the individual domains, the substrates, the adhesive, and the interphase regions. The weakest link of the bond, as described by the anatomy of a wood bond by differentiating nine zones within the bond from the pure adhesive film to the two wood substrates, determines the strength of the joint [115]. Marra considered the wood and adhesive interphases as the weakest zones compared to the bulk wood or adhesive or the adhesive-wood interface [115].

With regard to the viscoelastic behavior of the entire bond in service, the performance (e.g., deformation) in use depends on the sum of the performance of its individual components, or zones, and their individual viscoelastic contributions. Although the wood may creep, it is desired that the creep in the bondline be so small that it can be neglected.

In addition to the generic definition of the strength of a material being a measure of the maximum stress level resulting from external forces, adhesive bonds characteristically develop considerable inherent and internal stresses. The *inherent* stresses result from the bonding and curing process, originating from differences in expansion and contraction of substrate and adhesive (loss of solvent, shrinkage from the curing reactions, local swelling and shrinkage as a result of local moisture redistribution, thermal expansion, etc.) during bond formation and curing (setting) steps. Possibly even more important are *internal* stresses occurring, especially in wood adhesive bonds, as a result of exposure to environmental conditions and the generated stresses due to blocked swelling and shrinkage movements [345]. Compression stresses due to hindered swelling expansion of initially oven-dry wood are known to reach up to several MPa perpendicular to fiber direction. Tensile stresses perpendicular to the grain orientation as a result of excessive drying (occurring in the outer region of a bonded sample during drying in delamination tests) can reach considerable stress values (e.g., up to 6 MPa for beech wood [428], which is sufficiently high to cause weakening or even failure of wood perpendicular to the grain orientation, evidenced by resulting radial cracking). The capability of wood to generate significant stress levels due to swelling and shrinkage is considered in testing standards, e.g., delamination tests for solid timber applications [313, 432]. These test methods do not have any type of external loads and are considered as the most severe and challenging test methods for adhesives intended for use in structural applications of laminated wood [140, 164]. The delamination method itself comprises cyclic immersion of specimens under water in vacuum conditions (swelling) and

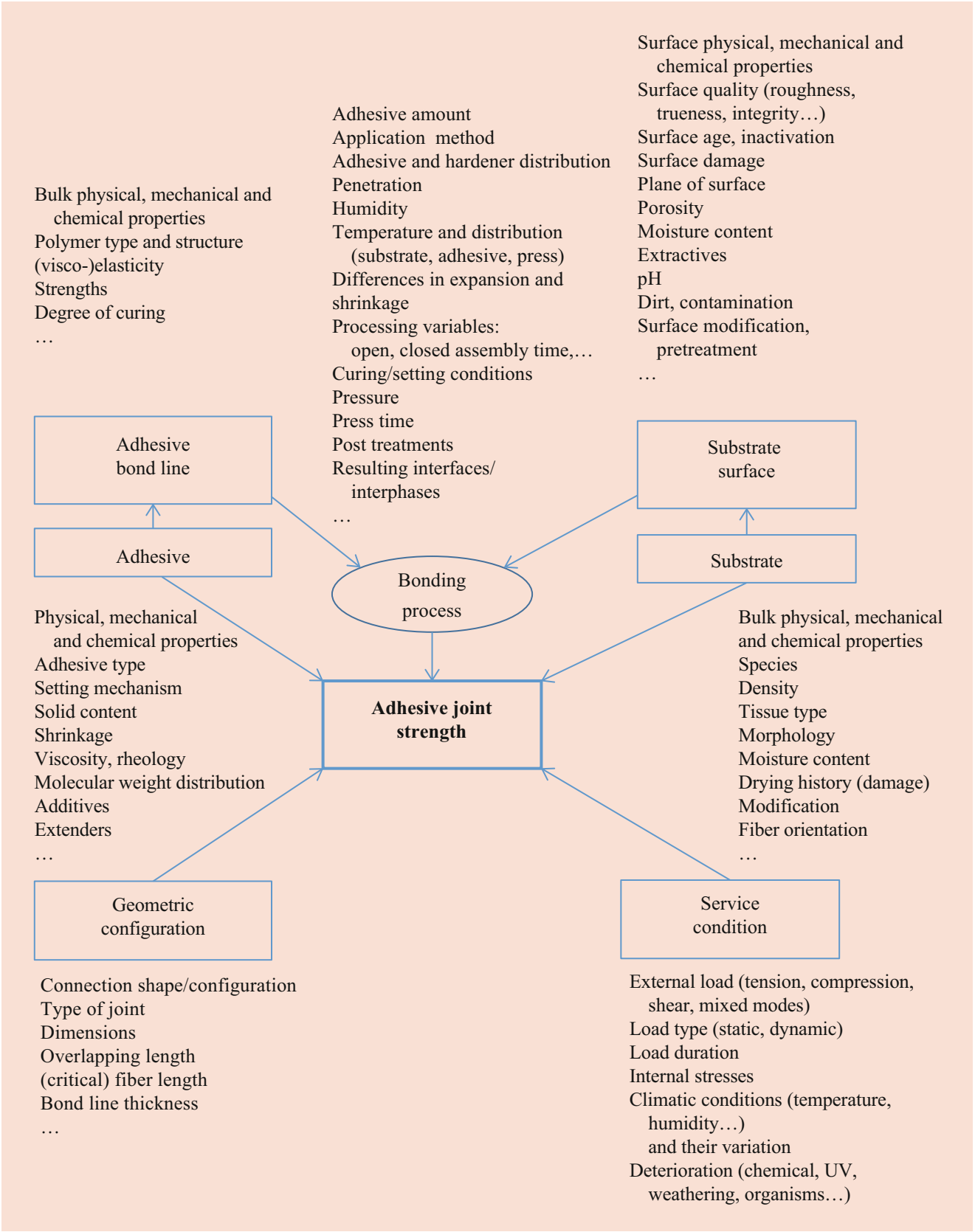

Fig. 14.29 Selection of influencing parameters for adhesive joint strength. (Adapted from Refs. [105, 132, 146])

subsequent fast oven drying at elevated temperatures. In addition to pure swelling and shrinking, exposure to high humidity levels and temperatures aggravates the reduction in strength of the wood as well as the adhesive, and consequently the joint.

In light of the importance of internal and inherent stresses present in wood adhesive bonds, the strength values determined by mechanical testing may be better described as *residual or apparent strength*, that have to be clearly associated with a specific testing condition. The apparent strength measurable by mechanical testing of a specific bond configuration is therefore the theoretical strength of a bond, reduced by the amount of inherent and internal stresses [345]. Due to the viscoelastic behavior of adhesive polymers, the magnitude of the strength of the individual components may change with time due to relaxation processes (stress reduction with time depending mainly on polymer type, temperature, humidity, and duration) [430].

Similar to adhesive strength, the strength of wood adhesive bonds determined by the many available testing methods is mainly used for comparative purposes and quality management, but rarely for design purposes because the normal performance of a bond product is measured on the product itself. Adhesive bonds and materials formed thereof have to exceed threshold values to comply with wood material and wood products standards. Furthermore, for many wood applications, the joint itself is usually not considered as an individually contributing member, as the performance of the final product (e.g., glulam, plywood, particleboard) formed by joining wood elements together is typically in focus.

In order to assess the quality of a bond and to consequently conclude on performance, reliability, and durability of various tests methods have been evaluated for relevance. The common measurement to estimate potential performance of bonded wood joints, in addition to strength, are wood failure and delamination, often after water soakings [429].

Wood failure and the mode of failure are frequently analyzed after specimens have been tested. The mode of failure is the locus in the bondline through which the failure propagates [433] and may be attributed to one of the links in an adhesive bond as described by Marra [115]. However, the analysis often focuses on percent wood failure over the entire bondline, rather than giving a detailed investigation of the exact location of failure [434]. Classical designation of the main failure types is performed by analyzing the failure pattern as harmonized in corresponding standards [435, 436]. Various shallow cohesive substrate and adhesive failure types are often described the same as adhesion failure, but closer examination often reveals that true adhesion failure is rare. Real adhesion failure is difficult to identify because it can be easily misinterpreted with shallow cohesive failure (in either substrate or adhesive) occurring extremely close to the interface or in the interphase, and appropriate techniques have to be used to identify the real failure mode. More detailed information can be found in corresponding literature [360, 433]. The influence of adhesive properties (brittleness vs. flexibility) on the failure mechanisms occurring in rather brittle UF bonds has been analyzed [155]. Hass et al. [437] investigated a wider range of adhesives and corresponding differences in mechanical properties together with various joint configurations and their influence on failure mode.

From occurring in use and in experimental applications, a classification to one of the following main loading modes will be discussed in the following sections. These basic loading modes are shear, applied by either external compression or tension shear forces, or normal forces, induced by either external tension, or compression forces as well as bending moments. As classical strength analyses do not account for the viscoelastic behavior of most adhesives, a corresponding section addresses this behavior.

Shear Strength

In general, adhesive bonds display their highest strength when loaded in shear [433]. Consequently, most adhesive bonds, especially structural products, are designed to make use of this advantage, such as laminated bonds or when using substrates with a greater length in the applied force direction. Concurrent to their use, multiple adhesive bond test types place the adhesive in a state of shear (an overview of ASTM test standards including wood and other applications can be found elsewhere [106, 433]).

A classical specimen geometry, and probably the most widely distributed one for wood adhesive related research and adhesive accreditation due to its simplicity, is the single lap shear specimen (see Fig. 14.30a) for determining the longitudinal tensile or compression shear strength of wood joints [438–440]. Passing the specific test requirements is a prerequisite for classification of nonstructural [441, 442] as well as structural adhesives [313, 443–448].

The advantages of this test setup is its simplicity and the capability of applying modifications in adhesive layer thickness (gap joints), as well as the possibility of exposing the specimens to different climatic conditions (temperature, humidity) and test durations. Slightly modified versions of the test geometry are also available for tests on laminated veneer lumber and plywood [449, 450].

Another veneer-based version of the tensile shear test is gaining popularity after becoming standardized [451] which tests the bond strength development influenced by the duration of hot pressing, see Fig. 14.30b. In contrast to the normal method of measuring joint strength, this small-scale method typically tests specimens immediately after hot pressing in hot or cooled condition, but omits conditioning of the specimens for several days in standard conditions. Parameters tested here are important for industries where curing speed, and consequently production throughput, is crucial (e.g.,

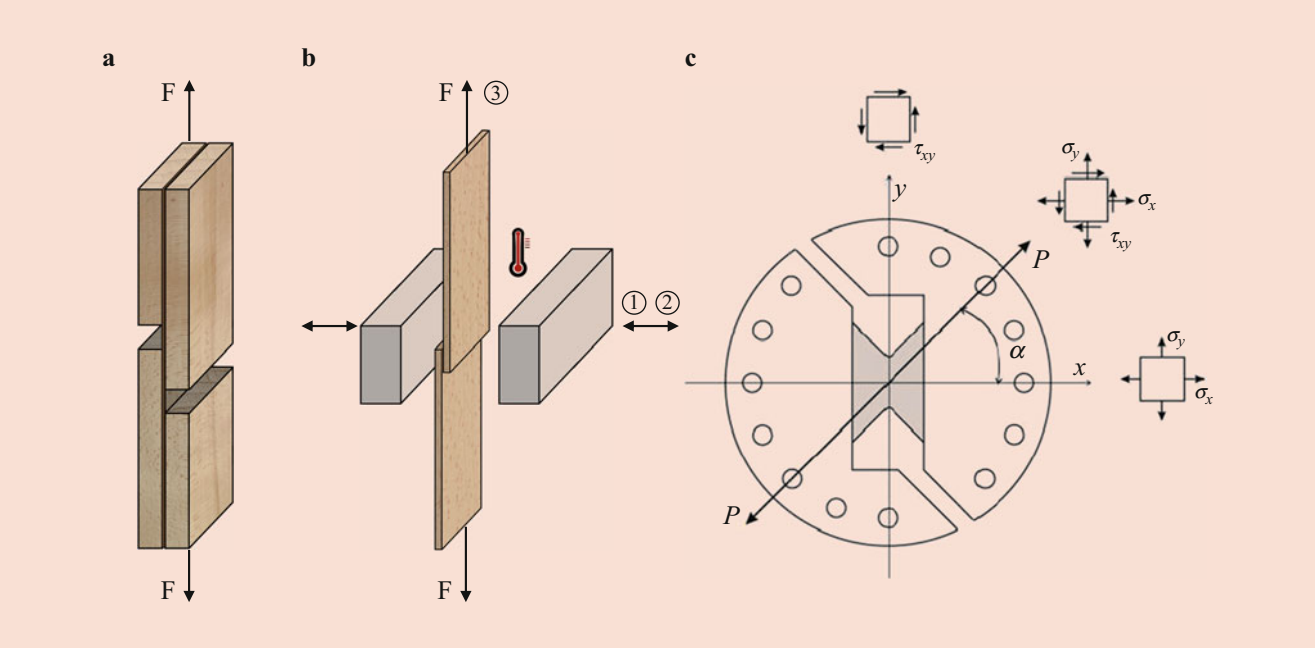

Fig. 14.30 Illustration of (**a**) a classical lap joint specimen using timber lamellas according to Ref. [438], (**b**) a systematic sketch of the small-scale method of Ref. [451], and (**c**) the Arcan shear test setup [427]

wood panel productions: particleboard, MDF, OSB). However, because of the thin specimens, the test does not replace accepted standard industrial performance testing methods.

Classical lap joint specimens tested to fracture are typically regarded as successfully passed when failure in the wood substrate is the dominate failure mode. This requirement is based on the assumption that the adhesive bond is exceeding the performance of the wood. Using a single wood species with defined density, typically a certain comparably homogeneous strength level is reached which is dominated by the mechanical performance of the wood (specific species and density) and may reach shear strength values in the range of 3–18 MPa [429, 452] under standard conditions. The measured strength is therefore a threshold value, limited by wood strength in the corresponding load mode and direction (wood shear strength parallel to grain), and does not necessarily represent the specific strength for the adhesive tested. The test is therefore regarded as an appropriate tool for ensuring a certain quality level. For a direct comparison of mechanical properties of adhesives and the bonds created therefrom [453], the informative value of the test is limited. This is especially true if the wood specimen is different from that used in the final application, because the wood used for the testing is clear wood pieces with a low grain angle. The European beech wood required for testing adhesives [438] exhibits high density with corresponding high shear strength, while the adhesives certified herewith are usually applied using softwood adherends. It has to be considered that several properties of beech wood (surface condition, penetration behavior, etc.) may significantly differ from the properties of the actual adherend. Consequently, it is reasonable to validate the performance of an adhesive using the wood species of the final application [452]. In order to better differentiate between adhesive performances, exposure to different conditions is performed as an accelerated test. Some of these conditions never occur in real products (water soaking, boiling water, re-drying, etc.), but will lead to weakening of the bonds of lower quality or lower resistance to simulate the effects of in use exposures over long time frames, such as years or decades.

For simplicity, stresses (strengths) occurring in lap joint specimens are calculated by dividing the applied (maximum) load by the corresponding original overlapping area [438]. However, characteristic for lap joints is a stress distribution with distinct peak stresses at both ends of the overlapping area. An early numerical approach to estimate the stress distribution within the overlapping area was proposed by Volkersen [454]. While the original approach considered pure shear deformation and elastic response of the substrates and adhesive only, numerous advancements and refinements of the method are available now. The substantial amount of bending of the substrates and resulting tensile stresses in the adhesive, as well as nonlinear elastic and viscoelastic material behavior are included in state-of-the-art analytical models. For detailed information on those advanced analytical approaches describing the stress distribution and its influencing factors, the reader is referred to corresponding textbooks [139, 360, 427].

Based on the original simple calculation by Volkersen, which has shown to provide meaningful values for wood adhesive bonds [455], the following major influencing factors on peak stresses observed in lap joint specimens are summarized [423]:

- Peak stress increases with increasing adhesive shear modulus
- Peak stress increases with decreasing substrate modulus, substrate thickness, and adhesive thickness
- Peak stress for long joints is independent of the joint length

In addition to these fundamental relations, peak stresses decrease with more pronounced plastic and viscoelastic deformation behavior (stress relaxation) [360]. Consequently, factors increasing plasticity of the adhesive to a higher degree than the substrate, such as higher temperature or humidity, may result in reduced peak stresses. Experimental observations by Marra [115] also showed the positive influence of adhesive plasticity on bond strength.

As a consequence of these influencing factors, a direct quantitative comparison of results obtained from different specimen geometries (Fig. 14.30a and b and as discussed in Refs. [313, 438, 456]) may not be meaningful, and should be made with great care only. In addition to the differences in geometry, temperature, and humidity of the adhesive and substrates influence their corresponding mechanical properties and other factors, e.g., differences in surface conditions of used veneers and lamellas (aged, fresh), also have to be considered that result in typically lower strength values for when testing identical adhesives [313]. Simple adaptations of test geometries (lamella thickness) necessary to avoid substrate tensile failure occurring with thermally modified wood may result in a lack in comparability to standard tests [457].

Another important test method is the compression shear test, often referred as the block shear test [372, 436]. This test has a long history in the development of suitable wood adhesives for solid wood applications in that it can be compared to the compression shear of wood in the tangential direction. This test is in use to assess bond quality of glulam elements for quality control as specimens can be easily produced out of manufactured glulam beams. A detailed discussion of the test can be found by Marra [115, 436]. Similar for the lap joint geometry, block shear test samples show distinct deviation from homogeneous stress distribution [458] and are assumed to be affected by similar parameters as described before for the lap joint test. While the fiber direction of both substrates is aligned in the same direction in a block shear test, other test geometries [459] require cross-alignment of the substrates. Such configurations can introduce considerable amounts of swelling and shrinkage stresses into the bond (internal stresses), but require a significant effort to produce suitable specimens.

Overcoming the restriction of dominating wood failure, scarf joint specimen geometry has been used for decades and has been a former standard method [460]. This method is representative for adhesive joints with related joint geometries like finger joint connections because penetration of adhesives into the wood is clearly biased by the inclination of the surface with regard to the fiber direction.

A specimen test was designed to provide a homogeneous stress field, with the additional capability of adjusting the direction of loading mode with regard to the main testing field, and the capability of testing even mixed modes is the Arcan shear test (Fig. 14.30c) as reviewed by da Silva [427]. Testing solid wood [461] verified the homogeneity of the stress field in shear mode, but until recently, only single applications of wood bonding related studies were available [462, 463].

Early and current test geometries used to investigate adhesive bonds are compiled in various references related to wood bonding [115, 365, 464, 465] or more general applications [425, 427], including the group of fracture tests based on shear stresses (Modes II and III) [466].

Tensile Strength

Tensile stresses exist in various joint configurations. End-grain joints (butt joints) loaded in longitudinal direction imply direct tensile stresses. Other joint configurations with forces applied perpendicular to the bondline also result in tensile stresses. These mechanical forces may be applied directly by pulling apart two surfaces, or by peeling. Alternatively, such forces can be applied by a wedge or other crack-opening device, or by pulling on a double cantilever beam [261, 467, 468]. While direct symmetric loading perpendicular to the bondline results in comparable homogeneous stress distribution as the beam is uniformly rigid, peeling or cleavage results in an advancing front of locally high and concentrated tensile stresses.

Other joints involve tensile stresses that are less obvious or unintended, as stress distributions in real joints are typically more complex than they first appear (e.g., lap joints). Additionally, tensile stresses as a result of local swelling and shrinking can be sufficiently high to cause failure, as described previously.

Tensile joints are avoided in design because it has been observed empirically that many adhesives exhibit lower strength and high sensitivity to alignment when exposed to tensile stresses [139]. Wood is extremely strong and stiff in the longitudinal direction. In order to safely transfer longitudinal tensile loads, a designer, especially when aiming for structural applications, can markedly increase the contact area of two substrates with the adhesive over that of a simple

end grain or butt joint by overlapping, scarfing, etc. As a consequence, typically joint designs are used that are capable of transferring longitudinal tensile loads into shear loads in the joint area (lap joints, scarf joints, finger joints, etc.).

Axially loaded butt joints are not simple to manufacture as any misalignment induces bending loads, and adhesives do not resist such loads as they put the adhesive in cleavage [427]. End-grain joint tests have been used for comparing, for example, different gluten-based adhesives decades ago [465]. For scientific purposes, end-grain joints are still used, as shown by a study investigating the theory of mechanical interlocking [469]. The authors observed improved bond strength for specimens with higher density, with comparable high average tensile strength values of approx. 15 MPa for a corresponding wood density of approximately 700 kg/m^3, along with a high degree of scattering. Even with special techniques, it is summarized that it is practically impossible to make end-grain butt joints sufficiently strong to meet the requirements of normal usage [429], as only about 25% of the tensile strength of the wood parallel-to-grain can be obtained with this joint geometry. Thus, butt joints have been replaced by either scarf or more commonly finger joints.

For assessing other aspects of bonding, tensile strength tests transverse to the fiber direction of wood are regularly in use [470]. These tests have been standardized for adhesives for load-bearing timber structures, for testing the effect of acid damage of adhesives or their components [471], and for long-term testing (glass house test) for adhesives other than cured phenolics and aminoresins [472].

The internal bond strength defined as the tensile strength perpendicular (normal) to the plane of a particle-, fiber-, or strand-based board is another example of an important standardized test method involving externally applied normal tensile stresses [473]. The latter is a convenient measure of the quality of the typically less dense core layer as a result of the adhesive bonding process.

While the stress transfer between adhesively bonded strands, veneers, fibers, or other elements with high aspect ratio of most wood composites is assumed to be mainly of shear type, some amount of normal (tension, compression) stresses may also occur, especially for composites made with particles of low aspect ratio. For wood plastic composites, shear stresses together with considerable normal (tensile) stresses have been experimentally detected, as reported by Sretenovic et al. [474].

Even for geometrically well-defined joints, tests, and applications, a certain amount of unintended tensile stress might occur. In the example of the well investigated stress distribution of a simple lap-joint specimen described in detail above [360, 427, 475], instead of a homogeneous shear stress field, a gradual distribution of shear stress is present that changes with the mechanical properties of the substrate/adhesive configuration. Due to the expected rotation of the substrate in the bonding area, a certain amount of tensile stress is present as well. Also for scarf-, finger-, and other joint configurations, a certain amount of tensile stress is overlapping shear stress in corresponding bonds.

Fracture tests are a further group of frequently used tests to investigate adhesives and their bond performance [466]. Among them, tensile stresses are in focus when performed in mode I, i.e., tensile normal opening loading conditions. Double cantilever beam and cleavage tests result in tensile stresses, and also the peel test with the difference of having at least one flexible adherend. Numerous applications of fracture testing using wood-based substrates and corresponding adhesives are available [462, 476–479].

An overview of different testing methods is given in various textbooks [107, 115, 365] including methods for investigating tensile strength, shear strength fracture mechanics, peel, and other tests.

Viscoelasticity, Creep, and Relaxation

Creep and relaxation describe the time-dependent and partially reversible behavior of viscoelastic materials exposed to long-term static loads following an initial instantaneous elastic or rapid deformation [480–482]. Creep *strain* and relaxation *stress* show the change in their magnitude with time. More precisely, creep describes an increase in viscoelastic deformation as a result of static stress, while for relaxation at static-strain conditions, creep-related phenomena in the material leads to a time-dependent reduction of stress [427]. Exceeding the viscoelastic range for nonreversible (plastic) deformations results in *flow* and finally leads to the fracture of a material. However, these creep and relaxation experiments are generally run under conditions far removed from bond failure conditions. Many bonded products are subjected to static stress ranging from a loaded bookshelf to floor joist in a warehouse.

The origin of this time-dependent behavior is based on a release of individual intermolecular (secondary) bonds and the resulting possibility of motion of the polymer molecules passing one another. Released bonds can be only partially reformed, leading to a loss in residual strength as a result of long-term loading [360]. Basically all polymers, including both polymeric substrates and polymeric adhesives, show viscoelastic behavior. The degree of change with respect to the time-dependent behavior significantly depends on the rigidity of the polymer backbone, cross-linking density (primary bonds), and the amount of secondary bonds present in the material. Consequently, the polymer type determines the polymer morphology and the time-dependent properties. As a general classification, thermoplastic polymers are much more prone to creep but not necessarily to relaxation compared to thermosetting ones, which have a higher cross-linking density. Additional parameters [360, 384] which highly influence creep rate are temperature and absorbed moisture in the

adhesive polymers [430, 483]. The effects of time, temperature, and moisture are analogous [425], but only time and temperature are related enough to be described by the superposition principle [484].

As a very general classification of adhesives used for wood bonding, thermoplastic polymers (e.g., PVAc and most natural glues) are most prone to creep and relaxation. Depending on cross-linking density, classical rigid polycondensation thermosetting adhesives (aminoresins, phenolic resins, etc.) tend to creep the least, while the creep is somewhat higher [485] for polymers with a comparably lower cross-linking density (PUR, EPI, etc.). With increased utilization of PUR adhesives [485], investigations on creep characteristics have increased dramatically in the field of wood bonding. Current trends in reducing the formaldehyde emissions for a range of wood products, together with the increasing availability of renewable-based alternative adhesive systems, may lead to adhesives with a different polymeric structure and a higher proportion of time-dependent material behavior. It is thus expected that investigating viscoelastic properties of adhesives will be increasingly important in the future.

For engineering products, it is important to estimate the expected deformations occurring during the lifetime of the product. Due to the typically high proportion (>90%) of the wood as such in wood-based materials, creep in design is mainly based on the creep characteristic of the wood. The adhesive bondline has not been considered as an individual element contributing to the creep behavior of most wood-based materials, although in North America the measured adhesive creep needs to be very low [481].

For adhesive connections in related fields (bonding of metal, fiber-reinforced polymers, etc.), evaluation of creep resistance has a longer history. Various coupon tests and standards have been developed to evaluate the creep resistance of adhesives [425], either by monitoring the time-dependent displacement of an adhesive specimen under load or by recording the time to failure. Predicting long-term performance, similar to estimation of time-dependent ageing effects of adhesive joints, is regarded as challenging due to the long time spans involved for testing [384]. As a consequence, accelerated tests are frequently used to reduce testing times. Similar to short-term strength tests as described in the previous chapters, viscoelastic behavior can be investigated using various tests on the pure adhesive, wood, or the bonded assembly. For pure adhesives that can be tested in bulk form, corresponding polymer-related standards are available [422, 486]. Creep of classical adhesives used for wood bonding was shown to be accessible in the form of films in different environments [483, 487]. Even within one adhesive type (PF), significant differences in creep behavior could be identified and were found to depend on resin pH [223], where resin alkali content was found to increase the hygroscopicity of PF adhesives resulting in enhanced creep.

Testing viscoelastic properties of pure adhesives present in the gluelines is also possible at the microscale using nano-indentation [248, 488, 489], as reviewed by Stoeckel et al. [490]. Similar to testing elastic properties of adhesives, the methodology has the advantage that adhesives can be cured in their typical environment (presence of wood, moisture, pressure, etc.), overcoming the challenge of producing isolated adhesive polymer film specimens, which may not represent the adhesive structure in the bonded wood product. Additionally, relative differences in creep behavior are accessible within seconds to single minutes of load duration. It is also possible at the microscale to investigate temperature-dependent elastic and viscoelastic properties of the adhesives [491]. In a recent study [430], micro-mechanical creep and relaxation behavior of some wood adhesives (UF, PVAc, EPI) were found to significantly change their properties with only moderate changes in MC. At smaller sampling volumes, the data may not represent the adhesive as a whole, but that of a specific domain within an adhesive.

For testing adhesive joints of non-wood adhesives, a range of standards and tests has been evaluated as summarized elsewhere [348, 427]. With regard to wood adhesive joints, in principle similar testing geometries as reported for shear or normal stress modes may also be used for investigating viscoelastic properties. As summarized by Knorz et al. [492], most standardized long-term test methods for structural wood products or adhesives mainly for determination of creep behavior (or time to failure) of wood-adhesive bonds apply either shear or bending loads [481, 482, 493–496]. Some of the test methods require rather long test durations of several months. For the shear test according to EN 302–8 [495], the maximum deformation recorded during testing time has to be lower than an indicated reference value. The four-point bending test proposed in EN 1546-3 [496] is a test comparing the creep behavior of an adhesive (e.g., PUR and EPI) to the creep behavior of a reference PRF adhesive. Discussion on reducing test durations, specimen geometry, and climatic conditions is still ongoing [497].

Viscoelastic properties of adhesive specimens and small wood adhesive bonds can also be investigated with the help of dynamic thermomechanical analyses (DTMA) using various specimen geometries. Dynamic loading of specimens combined with specific temperature and/or humidity control is an additional meaningful methodology to compare viscoelastic behavior of adhesives as evident by a range of examples [331, 485, 498–500].

14.2.4 Durability

All organic materials deteriorate or age according to their inherent structure and the surrounding environment [345]. It is therefore not surprising that durability in the field of wood adhesive bonding has always been a topic of importance. With regard to adhesive joints, the term durability is today defined as the endurance of joint strength relative to the required service conditions [501]. Vice versa, nondurability is a loss of initial strength over time. It is further specified that service conditions may include exposure to water and other chemicals, temperature, stress, radiation, microorganisms, and other environmental factors. It is regarded as comparably simple to achieve a certain initial strength value by adhesive bonding, but it is difficult to guarantee its permanence during the entire scheduled service life that can exceed many decades, while environmental conditions may change considerably. Examples of adhesively bonded artifacts have been found lasting for centuries or even several millennia, as evident from archeological excavations, e.g., in Egypt. However, most of the artifacts were in dry climates where wood swelling and shrinking are not an issue.

In earlier descriptions of durability-related issues, many terms have been used. Plath [465] used *ageing* and defined it as time-dependent change of elastic-plastic behavior of the adhesive layer in the bond, resulting in increased brittleness of the adhesive layer and consequently in reduced strength of the adhesive bond. River et al. [345] defined *permanence* as the resistance against deterioration of the bond with time, while the rate of deterioration may vary with time. They specified furthermore that a permanent adhesive, joint, or product shows no greater deterioration during its life in the service environment than solid wood of the same species does.

The importance of durability may be ranked differently for the various applications where adhesive joints are needed. In the middle of the twentieth century, durability of joints was of special interest for wood-based military and civil aircraft due to the immediate danger to the pilot and passengers. In contrast to earlier and current trends of replacing wood by other materials, today the increasing use of adhesively bonded engineered wood products for high volume and high rise buildings draws attention to static applications due to the potential of high consequences for the case of failure or malfunction (e.g., Eurocode [502] consequence class CC3: high consequence for loss of human life, or economic, social, or environmental consequences are very great). The importance of durability for the wide range of other applications both structural and nonstructural, such as interior furniture, may be different and should be evaluated for on a case-by-case basis.

The main factors determining the rate of adhesive bond degradation have been identified and are reviewed elsewhere [475, 503]. They can be grouped in three different categories: environment, materials, and stresses.

Environment for wood bonds is clearly dominated by temperature and humidity changes, but it could also include concentration of aggressive ions, various fluids, UV, other radiation, insects, and fungi.

Materials include the substrate (e.g., wood type, density, permeability, swelling properties, extractives, pH, etc.), and the adhesive (including its type, durability, possibility of hydrolytic degradation or other chemical degradation), as well as the interphase formed between them. This category includes the main factors described earlier for joint strengths, i.e., the appropriate combination of materials, as well as factors involved during joint production, such as wood surface preparation and conditioning, wetting capability, interface condition, and much more.

Stresses include the type and combination of stresses the joint is subjected to during its life time (typical stresses of tension, compression and bending, shear stresses, peel loads, etc.), the duration of loads, or the mode of stresses as static or dynamic. The joint design and mechanical properties of adhesive-substrate combination and the presence of stress concentration are expected to affect durability.

Due to the inherent properties of the adherend wood, the complexity of factors influencing durability is high. For most other structural (non-wood) joints and bonding non-swelling substrates, the main reason for joint weakening is again humidity and water entering at the interface [360, 504, 505]. In contrast to wood bonds, for such joints, critical humidity levels are available. Additionally, it is comparatively easy to estimate the rate of water diffusion using fundamental physical laws, and approaches for predicting lifetime similar to the Wöhler technique and identifying a "durability limit" are described by Pocius [506].

As moisture and heat are the most important factors in determining the strength loss of a wood adhesive joint, in the following sections special emphasis is given to describe the way humidity deteriorates wood adhesive joints. Due to an intrinsic lack of ability for predicting and estimating durability of wood-based bonds, methods based on accelerated ageing (e.g., delamination test) are used for ranking durability of bonds.

Moisture

Moisture is pervasive over much of the world and is responsible for the vast majority of bond failures, both in the field during service and in laboratories during research and development [503]. Brouse in 1938 used the term "destructive humidity" [362] to describe conditions that will ultimately cause failure of a glue joint. At that time, this was mainly important for natural glues, such as animal- and vegetable-based ones, including casein and blood, where environmental

conditions resulting in wood MCs above 17–27% were identified as destructive for the adhesives. Synthetic adhesives can also deteriorate with humidity. Hydrolysis is a well described effect primarily observed for UF adhesives [507], resulting in a loss of cohesive bond strength of the adhesive polymer. The effect is accelerated when combined with elevated temperature, time, and low pH values [508]. Additionally, mechanical effects can also cause loss of integrity, such as the UF's inherent brittleness propagating of preexisting cracks during moisture-induced movements that reduce bond strength [161].

Generic mechanisms by which water may enter a bond are summarized by Custodio et al. [475] and cover:

(i) Diffusion through permeable substrates; for wood bonds, this is likely to be the most important pathway in the beginning
(ii) Diffusion through the adhesive from the exposed edges
(iii) Transport along the adhesive/substrate interface; the latter two modes are considered to be more important for joints with non-permeable substrates, like metals or glasses
(iv) Migration via capillary action along cracks and crazes in the adhesive, the substrate, or in composite materials with a certain porosity

In the beginning of the lifetime of a wood bond, most of the processes described are reversible, such as seasonal climatic changes resulting in swelling and shrinking of wood and adherend, and the resulting induced stresses may be reduced by relaxation within the wood. With increasing lifetime, irreversible physical, mechanical, and chemical processes may result in permanent damages in the bondlines and decreased residual strength usually occur [509].

Apart from chemical degradation (e.g., hydrolysis) as mentioned before, humidity and water affects a joint in two main modes. First, the absorbance of water in both the wood and the polymeric adhesive alters a range of physical and mechanical properties. Polymers typically soften at higher MC and result in weaker joints. The effect is attributed to the weakening of secondary forces in polymers due to increased distance between molecules. For wood, this effect is very well described in several textbooks [428, 510]. Wet/dry comparisons of some selected wood-related adhesives was summarized by Stoeckel et al. [423]. Even thermosetting adhesive polymers showed changes in modulus and other mechanical parameters, but the results were not uniform with polymer type. Wood adhesives are frequently modified by different additives (e.g., fillers, extenders, etc.) [334, 343], some of which also possess hydrophilic character; these materials are expected to influence the moisture absorbance of the adhesive polymer. The influence, in a more narrow humidity range, on mechanical behavior of different structural [431, 511, 512] and nonstructural [430] adhesives has been demonstrated. Almost all adhesives, including the thermosetting polymers, were clearly effected by humidity, but the concern is about those with greater sensitivity.

The second main effect of moisture is the swelling and shrinkage of the wood. The degree of swelling/shrinkage with moisture changes is different for adhesive polymers and wood; the anisotropy of swelling/shrinkage in wood induces oriented stresses to the bond, which can be very high, and may weaken the bond or even result in failure [345]. In the example of the expected deformation of two wood lamellas as a result of moisture increase, possible swelling stresses occurring in bonds are visualized [140] in Fig. 14.31.

When wood is subjected to moisture, it will normally swell, and conversely it will shrink under dry conditions. An adhesive layer placed between two wood pieces, but unbonded, will not restrain dimensional changes in the wood, as illustrated in Fig. 14.31a. However, when bonded, the adhesive tries to restrict the dimensional change in the wood. Normally, the wood wants to return to its original shape, creating a compression force in the center of the radial direction and a tension force at the edge. At the same time, the wood is trying to expand in the tangential direction while the adhesive is retaining the expansion, creating a tension force within the adhesive and a compression force within the wood. In addition to the illustrated normal (tension, compression) stresses in the different spatial directions, distinct shear stresses will occur, especially in regions where a gradient in normal stress is present. In the example of the two bonded lamellas in Fig. 14.31, the highest shear stresses are expected in the horizontal direction parallel to the bond directly in the interphase (at the zero point of normal stresses).

All the mentioned stresses are superimposed by an additional stress arising from humidity gradients in the longitudinal direction of the lamella (Fig. 14.31b). The latter effect is especially relevant for mechanisms responsible for the failure of delamination tests or at the front end of beams. In these examples, the respective stress direction depends on the direction of moisture transfer. During delamination tests, the results of these stresses become visible after the drying cycle in the form of several cracks in the adherend, and undesirably in the bond region, visible at the cross-sectional front end of the delamination specimens.

As explained in Sect. 14.2, the different adhesives respond differently to these forces, resulting in two different classes of adhesives: in situ polymerized and pre-polymerized. However, the wood structure plays an important role in influencing the bond performance. The degree of swelling varies with wood species, with generally denser species swelling more when wet and then shrinking more when drying [345, 510]. This effect was shown comparing different wood species bonded with epoxies where white oak (0.72 specific gravity),

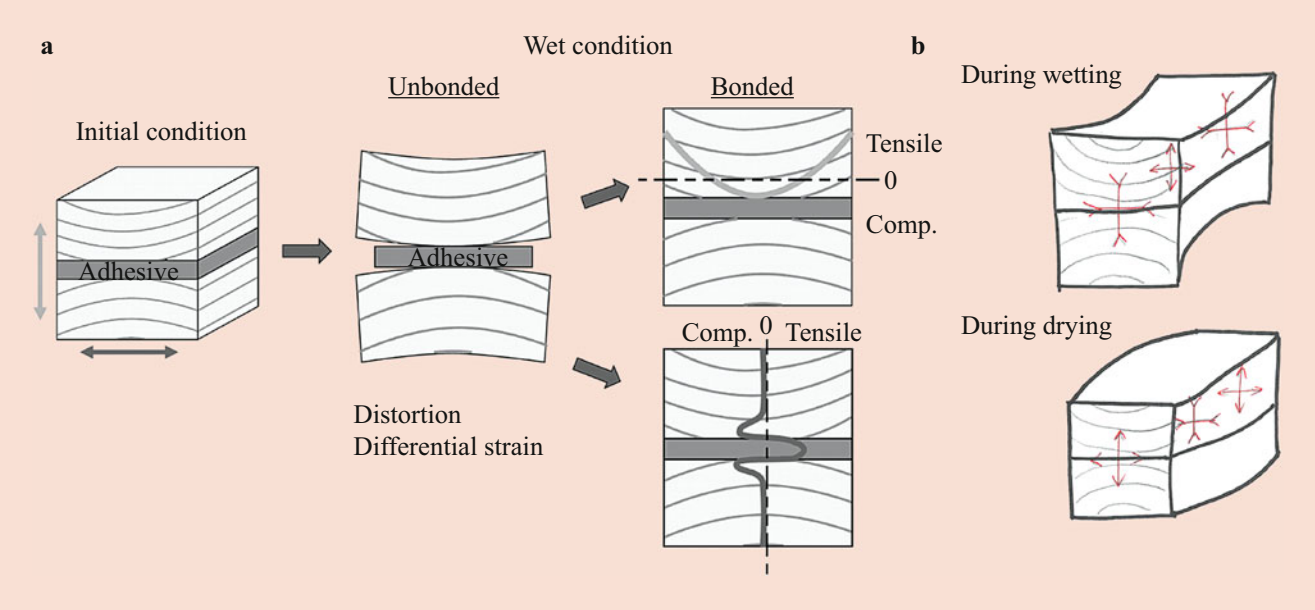

Fig. 14.31 (**a**) The effect of moisture on stress for unbonded and bonded wood showing that moisture changes alone can lead to bond rupture due to internal stresses. (**b**) Gradients of dimensional changes during wetting and drying (e.g., during delamination tests) indicated by different cross-section areas, resulting in additional compression and tension stresses (red arrows) of opposite direction, when comparing center and front end. Shapes of the originally cuboid are for visualization but do not reflect the absolute magnitude of the deformation or strain [133, 374, 375]

hard maple (0.66), and southern yellow pine (SYP) (0.54) gave high delamination rates after soaking and drying while Sitka spruce (0.41) gave none and aspen (0.40) was about 10% [141, 513]; thus, the lower density wood showed less swelling and showed more "durable" bonds. In developing PF adhesives, a lot of effort was required for good performance with SYP because of the large density difference between earlywood and latewood due to difference in penetration [514]. Examination of veneers stored for a while shows that some develop a very wavy texture that the adhesive needs to restrict to maintain flat plywood surfaces, although the steam and heat from pressing can reduce this problem. The cracking of wood at fast drying temperatures is well known [510] as most accelerated tests use fast drying conditions. In addition, the fast water uptake during water soaking limits any relaxation in the wood structure. Thus, it is clear the conditions of the accelerated tests provide a greater impact on the adhesive than normal exposure does per each cycle, but natural exposure generates many more cycles than do most accelerated tests. However, the most thorough comparison of bond performance between accelerated exposure and exterior exposure showed a good correlation for a variety of adhesives [167].

Besides such models whose purpose is a better understanding of generic mechanisms occurring in wood adhesive joints, more complex approaches to estimate the behavior of certain adhesive joint configurations and wood/adhesive combinations have been proposed as well. As one advanced example, an experimentally validated simulation of moisture-induced damage evolution was conducted by Hassani et al. [515] who applied different strain components such as viscoelastic, mechano-sorptive, plastic, and hygro-elastic deformations under changing MC for laminated beech bonded with different structural adhesives. Geometrical factors were considered as well. The stress buildup under cyclic wetting/drying loading was shown, resulting in hygro-fatigue. The importance of lamella thickness seems to agree well with investigations using beech [516] and observations made for very old timber structures exposed to high numbers of humidity changes [517]. Niemz [518] additionally pointed out the frequently underestimated importance of extremely dry ambient conditions occurring in protected indoor environments (e.g., behind glass facades or for heated floorings).

Heat

There are two cases of elevated temperature relevant for adhesive bonds and the products made with them. The first case is due to naturally occurring environmental reasons, which include higher ambient temperatures such as those found in attics, glass covered wood constructions, vehicles, and other applications. Custodio et al. [475] indicated that a typical range of −18 to 65 °C with higher temperatures up to 70–80 °C has been reported. The second case is single high temperature exposure during a fire. For the latter, the temperature inside of solid wood materials with bigger dimensions

was limited to approximately 100 °C [428] due to the presence of moisture and the developing charcoal layer, which acts as an insulator. Closer to the surface, significantly higher temperatures may be expected. While the first case is directly relevant for long-term durability, a fire is relevant for single exposure, and thus, is not regarded as a durability issue in Europe. In contrast in North America, the emphasis has been on the adhesive having the same heat stability as the wood [519, 520]. This fire heat-resistance is of current interest because of the construction of tall wood buildings and use of cross-laminated timber [296, 299].

Temperature alters the mechanical properties of both the wood and adhesive polymers. The well-known effects of short-term temperature changes on a range of wood mechanical properties can be found in different textbooks [428, 513, 521, 522]. The change in mechanical properties caused by temperature is significantly intensified at elevated MCs. For example, compared to room temperature for wood at 60 °C with high MC of 20% its loss in modulus of almost 30% can be expected, while for the same temperature, a loss of only 10% is expected at an 8% MC [428]. Additionally, a long-term duration of elevated temperature results in degradation of wood and a considerable permanent loss in mechanical properties [402, 403, 407, 410, 523].

While the influence of temperature on the wood is comparably well investigated, only some selected data on mechanical properties of pure adhesive polymers are available; in the past, the general expectation was that the thermoset adhesives used for engineered wood products would not have reduced bond strength more than wood does when exposed to elevated temperatures in unprotected assemblies for cases of short-term exposure [524]. For newer adhesives different from the classical phenolic- and amino-based adhesives historically used for structural wood bonding, research effort on investigating the temperature behavior of wood adhesives has been intensified. Some of the limited data on temperature-dependent mechanical behavior of pure adhesive polymers is summarized by Stoeckel et al. [423]. Between 20 and 70 °C, the range was from a slight modulus increase to a reduction up to 25% measured for typically highly cross-linked amino and phenolic adhesives. Increased moduli were also observed by others [431, 512], probably due to increased polymer mobility that leads to greater cross-linking. In contrast, the newer adhesives, including PUR and EPI, performed differently for the various adhesive mixtures tested. The modulus losses ranged from single digit percent up to a total loss in modulus at 70 °C. Thermal behavior of PUR adhesives was found to depend on the formulation of adhesives. Here the chemical structure of the prepolymer and the crosslinking density achieved represent modification tools [475, 524–526]. Furthermore, the thermal behavior can be modified by additives. Organic fillers like styrene acrylonitrile or polyamide showed increased cohesive strength over a wide temperature range similar to inorganic fillers (e.g., chalk) [527–529]. For EPI adhesives, the modulus was found to strongly depend on the formulation used and the loss ranged from very low up to 90%. With the choice of emulsion (e.g., poly(vinyl acetate) with different degrees of hydrolysis to produce poly(vinyl alcohol), ethylene vinyl acetate, copolymerized vinyl acetate-acrylate, acrylic-styrene, or styrene-butadiene rubber and modified versions of those are available) together with the choice of cross-linker (different polyfunctional isocyanates) and fillers (mainly calcium carbonate and other organic and inorganic substances), the degree of cross-linking and consequently modulus and heat resistance can be modified. Detailed information about EPI performance can be found in the previous Sect. 14.2.2 Emulsion Polymer Isocyanate or in a review [530]. Not surprisingly, a 100% loss in modulus for thermoplastic PVAc was mentioned in Stoeckel [423]. Others also report that increased temperature may result in "further cure," especially for cold curing EPI and PUR, resulting in increasing strength but reducing toughness of bonds [519].

Custodio et al. [475] concluded that in the long term, adhesives and the bonded products will degrade at a rate determined by the temperature, moisture, and the level of applied stress. For cured urea-formaldehyde adhesives, this degradation is well-known and attributed to a hydrothermal hydrolysis process (see also Sect. 14.2.2 Amino Type Adhesives) also involved in formaldehyde emission from this adhesive group [334, 507, 531, 532]. Combining temperature exposure, elevated humidity, and mechanical loading, urea formaldehyde adhesives degrade and embrittle in a way which does not allow for considering them as moisture resistant or structural adhesives. A considerable improvement of hydrolytic stability can be reached by modifying urea formaldehyde adhesives with melamine or phenol. This modification typically affects both thermal stability and emission. It was proposed to use hydrolytic decomposition to enable recycling of UF bonded materials [533]. Melamine-based adhesives increase their stability depending on their melamine content [334]. Phenol formaldehyde adhesives are considered to be relatively stable up to a temperature of 200–250 °C. The lower molecular weight components of the polymer degrade prior to the higher molecular weight polymer components, resulting in degradation occurring over a broad temperature range and finally rapid decomposition at about 400 °C [160, 219].

For most other adhesive polymers used for wood-based materials, data describing the rate of degradation is limited, but it is assumed that some degradation effect is also evident for these adhesives, similar to most other polymers at elevated temperature and even more if moisture is elevated.

Durability Testing

For any application, it is desirable to estimate predict durability. This is extremely difficult, as most of the factors influencing it are not exactly known for a specific application in advance. The factors that cause degradation are water and water vapor, heat, cyclic internal stresses, static and dynamic external loads, microorganisms, air pollutants, and ultraviolet light. The intensity of each factor varies in a given service environment, creating an infinite variety of degradation processes [345]. Therefore, Frihart [534] regards the principle factors to be heat, moisture, and stress combined with the adhesive's inability to withstand the swelling and shrinking of wood with moisture changes [109]. As durability assessments in ambient conditions would involve an unacceptable amount of time, a typically applied strategy is to simulate durability with accelerated test methods. These tests represent some form of extreme tests, unfortunately many being mainly empirically derived [535]. Typically, abnormally rapid and extreme moisture exposure or cycling is involved [534]. It is still discussed whether a single or a few cycles of high amplitude strain caused by rapid wetting and drying of the wood in the accelerated tests adequately simulates the slower wetting and drying in actual end use, due to the missing stress relaxation that occurs during slower natural climatic cycles. However, the available data have generally supported by some relationship being the tests and actual performance [470, 475, 517, 536, 537], including the most rigorous test involving three exterior test sites in the United States using a wide variety of adhesives [167].

However, the quality of correlation between accelerated tests and performance in service life is discussed with views ranging from being generally good to being impossible [107, 140, 167, 535]. One boundary condition for a consistent predictability is that failure mechanisms have to be the same for both long-term use and accelerated test results [538], and most papers do not cover the mode of failure. If there is a difference in failure mode, the accelerated test will not be a reliable predictor of long-term performance. Additionally, the joint design and concentrations of possible peak stresses should be representative for the joint in use [475].

If they cannot always predict long-term durability, at the very least such accelerated tests should provide some form of relative ranking of performance of different specific adhesive–adherend combinations, including the applied joint preparation used, or to distinguish between acceptable and unacceptable wood adhesives. It is important to realize that some of the older adhesives have been shown to hold up for many decades, but the wrong adhesive does not hold up when the end use changes to a more humid environment [539, 540].

Dinwoodie [535] categorizes three main groups of accelerated tests: single exposure tests, cyclic exposure tests, and mechanical tests. These tests typically incorporate one or more of the principle factors determining durability. The importance of measuring the durability of adhesively bonded wood products in most countries is evident by the enormous number of standard testing procedures referring to this type of performance. A range of typical standardized test methods is reviewed in several references, focusing on moisture-related durability, including tests using wet conditions and cyclic testing [140, 464, 541], some investigating the correlation with natural exposure [167, 535, 536], or including heat-related durability [345]. The importance of swelling has been observed in various studies; thus, delamination tests [168, 225, 313, 456] are among the most severe test methods, providing reasonable rapid assessment, with the advantage of including the swelling and shrinking properties of the wood species of final use. In addition, the acceptance of the accelerated tests has been shown to provide good wood assemblies in service. It has been assumed that these tests will also work in cross-laminated timber and tall wooden buildings.

Test methods focusing on heat-related durability are described by Craft et al. [542] comparing different US and Canadian tests methods using elevated temperature referring to both creep and strength. Standardized tests such as hot shear blocks [519, 543] combined with information from dynamic mechanical analysis and creep measurements [210] were used by O'Dell et al. [331]. The European heat resistance test (HRT) according to EN 14292 [544] was assessed by Richter et al. [485] using a bending test with lap joints, applying a temperature ramp, and correlating to dynamic thermomechanical lap-joint tests [500].

14.2.5 Non-adhesive Bonding

Because the adhesives are more expensive than the wood, there has always been an aspiration to make bonded products without an added adhesive. Usually the intent is to plasticize the wood, especially the lignin portion, to develop a bonded product that has sufficient strength, but none have been as well studied as frictional welding covered in Sect. 14.3 of this chapter.

14.2.6 Future Needs

With the availability of wood in most countries around the world and the ability to harvest trees to make wood products efficiently, wood will continue to be a readily available resource. Changes in climate and pest infestations

have continued to be a problem that decreases the supply, but in the United States, more wood mass is growing annually than is harvested. This is not as promising in the current market place since much of it is small diameter and not the desirable old growth. There is competition for the wood resources from the wood-to-fuel market that has been driving up wood prices. However, adhesives are the best way to efficiently use the wood resource because even sawdust can be converted into a commercially viable product.

With the market supporting tall wood buildings and unique designs for wood products, the need for high performance adhesives continues to grow. The continuing intelligent empirical studies are very important to overcome lack of understanding on the detailed interactions of adhesives with wood and adhesive strength to sufficiently allow for designing structures through the adhesive bondline. Given the lack of resources for empirically designed products, fundamental design methods may be an important limitation for developing the most economical adhesives and processes, along with improved knowledge of how accelerated tests relate to in-service durability.

Wood is considered a green material, leading to the emphasis to make adhesives from bio-renewable resources to make them even greener. Strong emphasis has been placed on studies on the use of proteins and low value lignin, but the commercial impact so far has been minimal due to the excellent performance of synthetic adhesives. Wood products perform well on cradle-to-grave analysis, but they are not as good on cradle-to-cradle analysis (circular economy) due to the low recycle of wood after consumer use. In some life cycle analysis methods, this is a drawback for wood since competing materials, like steel, aluminum, and concrete, have in-place methods for recovery of these materials at the end of their lifetime.

Acknowledgments At the FPL, we thank Linda Lorenz, Chris Hunt, and Daniel Yelle for their contributions, along with Manfred Dunky and Tony Pizzi for their fundamental and commercial insights.

14.3 Linear Friction Welding of Wood

The linear friction welding of wood is an innovative technology that has been developed by different international research teams during the last 10 years. The major motivation for this development was the lack of a sustainable and fast assembling technology for the bonding of solid wood for indoor application. Standard bonding technologies are based on the use of petroleum-based liquid adhesives. Moreover, these systems need a long assembling and pressing time and in many cases a curing under heat is required.

The first attempt to weld wood was carried out in Germany in 1996 [545]. In 2001, Gliniorz reported on the utilization of the friction welding for wood-to-wood welding as an innovative process with high potential for development [546]. In 2002, the first attempt in wood welding by linear vibration friction welding was carried out at the Bern University of Applied Sciences, Institute for Materials and Wood Technology [547]. The results indicated that linear vibration can also be used to induce wood-to-wood welding, hence to manufacture high-quality, environmentally friendly wood joints made without any adhesive or any additional chemicals.

Over the years, the technology has been improved and has reached a very high level of performance at the laboratory scale (up to a welded surface of 1600 cm^2). Even though the process is not yet established at the industrial level, interesting perspectives have been highlighted in different application fields.

The following chapter will describe the major achievements and the most important technological aspects of this technology as well as the properties of the products obtained with this fast assembling technology.

14.3.1 The Process

The linear welding process is a technology using the combined effect of pressure and friction. When both parameters are applied on two solid wood pieces, a fast increase of the temperature at the interface of the two pieces can be monitored, as can be seen in Fig. 14.32.

The welding frequency and the amplitude play an important role during the process. Most of the investigations have been carried out at a frequency of 100 Hz and an amplitude of 3 mm, these parameters being most of the time defined by the machine design (the frequency being given by the design of the electromagnetic spring in the case of Branson machinery). The use of a higher frequency of 150 Hz has shown some improvement regarding water stability [548].

Other important parameters in the welding process are the holding time and the holding pressure. All these parameters are interconnected and strongly dependent of the wood species. Regarding wood quality and wood preparation, kiln-dried wood having been planed and stabilized at a standard humidity (wood humidity around 12%) gives the best results. A high moisture would lead to low friction forces and consequently to a slow increase of the temperature. A very low wood humidity would create an excessive material burning.

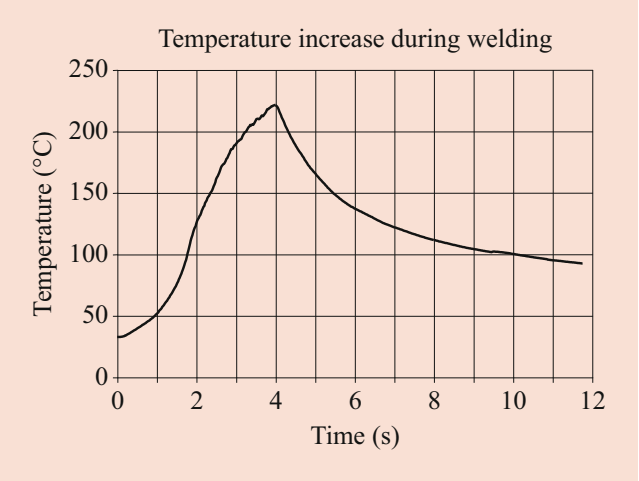

Fig. 14.32 Profile of temperature increase during welding for a join manufactured with wood cut in the longitudinal radial (45°) grain orientation with a welding time (WT) of 4 s. (Source: Ref. [559])

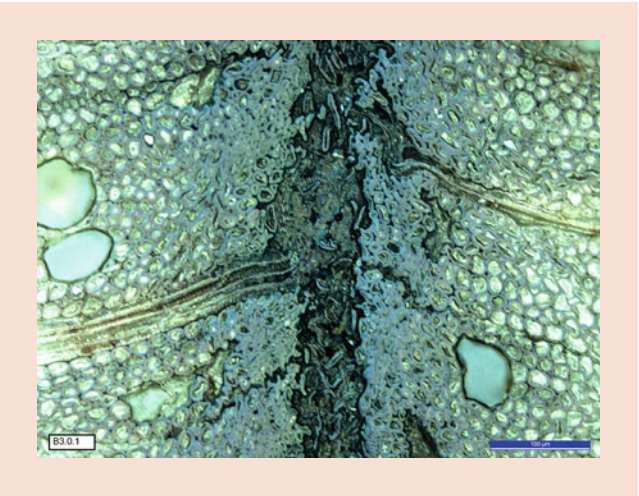

Fig. 14.33 Microscopic view of the welded line. (Source: Bern University of Applied Sciences)

The formation of the welding line (Picture 1) can be described as follows: it was found that during welding, extensive solid-state transformation phases occur in the so-called melting zone and the heat-affected zone. The nature and the extension of such transformations are correlated to the energy input and thus to the heat generated during the process at the wood joint interface as can be seen in Fig. 14.33.

During the melting process, lignin material is softened and wood fibers are being strongly deformed. The cooling step under pressure leads to the formation of a new composite material being composed of melted lignin and strongly deformed wood cells (Fig. 14.34).

Thermal conversion starts and damage to wood structures is visible at temperatures above 200 °C (WT 3–4 s). True pyrolysis begins at temperatures higher than 270 °C. Thus, based on the maximal temperature (MT) values measured, it can be assumed that both melting and thermal conversion of wood components occur during welding.

14.3.2 Mechanical Properties, Water Resistance, and VOC Emission

The energy input, and thus the heat generated at the joint interface, plays a key role in the chemical/physical processes leading to the final strength of the welded joint.

One of the main results is the increasing content of Klason lignin and decreasing amount of carbohydrates with welding time. Klason lignin represents the modified lignin that has probably partially reacted with decomposition products from hemicelluloses [549]. The amount of lignin in the composition influences the mechanical properties of the welded joint. The ratio Klason lignin/carbohydrates (hemicelluloses plus cellulose) follows an increasing trend. The reason for these increasing ratios is evidently the simultaneous effect of rise of temperature and continuous "mixing" of wood components during the time that frictional movement is applied. Temperature and mechanical friction produces the depolymerization of hemicelluloses, lignin and in small amounts cellulose, and allows the reactions among the depolymerized fractions.

In all the investigations, the mechanical resistance of the welded joint has been measured according to the European standard EN 205 [550].

Table 14.1 gives the tensile strength of welded maple samples in relation with different grain orientations. As can be seen, the fiber orientation has a strong influence on the final shear strength.

Other investigations have put in evidence that the welded joint is characterized by a fragile rupture mode, this property being given by the presence of melted lignin at the interface [551].

A consequence of this joint property is a limited application of the technology in the field of load-bearing structure like glue-laminated timber. A second limitation of the process is related to the solubility of many decomposition compounds. When being exposed to a high moisture content or water, the welded joint undergoes a chemical decomposition, the soluble compounds being extracted out of the joint. Furthermore, the residual strength being locked in the strong densified wood cells tends to recover at high humidity. The combined effect of tension release and dissolution of degradation compounds lead to a rapid delamination of the welded line.

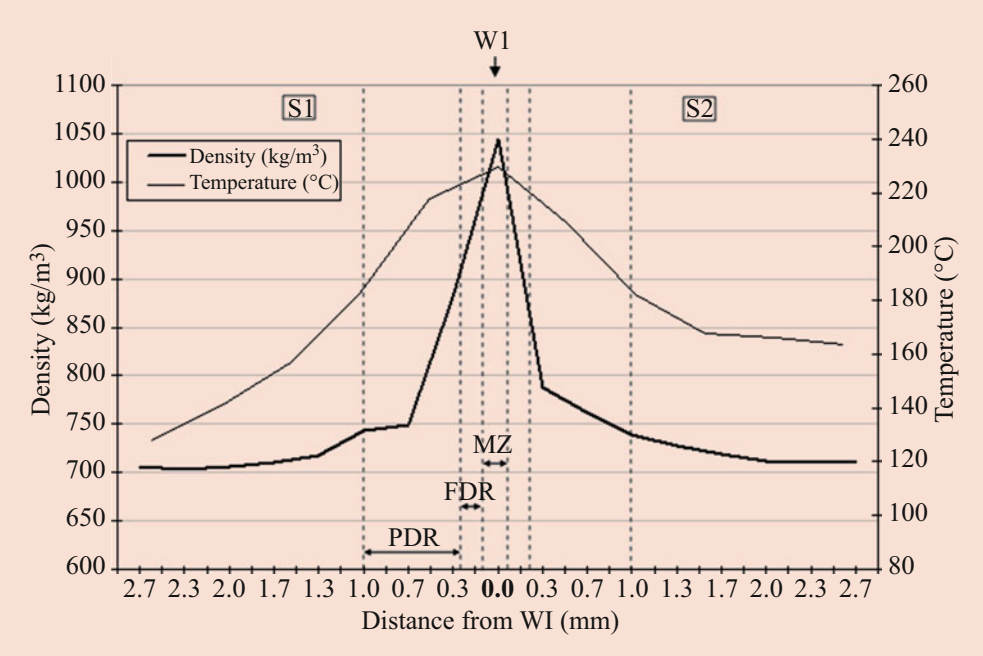

Fig. 14.34 Density profile, microscopy image (transversal cut), and temperature distribution perpendicular to the welding surface for a joint manufactured with wood cut in the longitudinal radial (90°) grain orientation, showing the welding interface (WI), heat-affected zone (partially deformed region (PDR), fully plasticized and deformed region (FDR), and melting zone (MZ) [559].

Table 14.1 Tensile-shear strength (TS) according to European Standard EN205, with maximal temperature (MT) and maximal average temperature (MAT) measured after 4 s of welding at a different average temperature increase rate (TIR)

Species	Grain orientation	TS (MPa)	MT (°C)	MAT (°C)	TIR (°C s^{-1})
Maple	Tangential (0°)	6.5±1.6	265±3	216±6.4	45.7
Maple	Radial (90°)	8.1±0.8	284±8	223±10.5	47.5
Maple	Radial (45°)	9.0±0.9	282±13	223±6.2	47.5

Each result reported in the table is the average of 10 tests ± standard deviation

VOCs (volatile organic compounds) of the smoke during the welding process are mainly composed of decomposition products of hemicelluloses and very little from lignins [552]. This goes along with the mass balance of welded material that shows an increasing amount of Klason lignin in the welding interphase. VOCs and aldehydes analyses on welded panels of beech and spruce show that no harmful chemical compound is present in concentrations exceeding the maximal allowed values for internal applications.

14.3.3 Increasing Mechanical Performance and Water Resistance of the Welding Line

Looking at solutions for improving the resistance, the addition of natural fillers can have, under a certain extent, a positive effect on the final strength of the welded connections. To this regard, it has been found that the pretreatment of the specimens with a cross-linked polysaccharide (Levan) can enhance the tensile-shear strength of the joints from 8 to 10 MPa. By contrast, the addition of both CMC (carboxymethyl cellulose) and lignin does not improve the mechanical quality of the connections.

It has been discussed previously that an important amount of the welded material is soluble, which explains in a good extent the instability of the joints to water. Among the identified-quantified water extracted components in water, there are lignin fragments, decomposition products of hemicellulose as monosaccharides, i.e., xylose, cellobiose, mannose; polysaccharides, acetic acid; and even some anhydrosugars as levoglucosan that come from the decomposition of cellulose, probably the amorphous part.

The feasibility of improving the resistance of welded joints of beech to water was tested by using different natural additives. Additives were selected based on their hydrophobic character which would improve the hydrophobicity of the welded joint. Some of the used additives are listed here [553, 554] below:

- Acetylated lignin
- Acetylated lignin modified
- Organosolv wheat straw lignin
- Organosolv wood lignin

- Rosin ester (colophane, a natural resin extracted from some softwood species), commercially available
- More recently, the use of citric acid has also been reported [555]

All lignins (acetylated or not) were applied as powder in a thin layer over one of the two wood specimens before welding. Rosin ester was impregnated in ethanol solution in both surfaces of the wood specimens followed by a drying step before welding. In general, with all types of additives employed, a relative improvement of the joints to liquid water was observed. In the best case, the joints soaking in water after 12 h still had about 67% of their initial shearing strength, which was measured after drying-acclimatization of the joints. In contrast, joints welded without additives get opened in the welding interphase after 0.5–3 h of water soaking. However, all welded joints with additives have a lower shearing strength (at 50% RH and 23 °C) compared with welded joints without additives (6 ± 1.2 MPa, compared with 8 ± 1 MPa) [556].

It has to be mentioned that welded wood samples stabilized at a humidity of 12% do not exhibit any joint delamination over the years. Finally, the coating of welded wood pieces with a commercial transparent coating can offer the best protection against water and humidity.

14.3.4 Welding of Wood-Based Panels and Heat-Treated Wood

Investigations on heat-treated wood indicate that such a treatment can give good strength results but, in general, the values are lower than that obtained with untreated wood as indicated by the birch and beech untreated controls [557]. This is expected because cell wall degradation induced by heat treatment is well known to induce lower strength and greater brittleness of the treated wood. Heat treatment of timber especially decreases the tensile strength of wood (cellulose hydrolysis causing cleavage of the fibrils), whereas its compressive strength (and hardness) is slightly improved (due to an increased cross-linking of lignin due to chemical reactions the lignin undergoes under heat treatment).

Other investigations [558] have demonstrated that panel products such as particleboard, OSB, plywood, and MDF panels can be welded to have good bonding strength by linear vibration mechanical welding. Edge-to-edge panel welding gives better strength results than face-to-face welding. The properties of the welding line being strongly correlated to the mechanical properties of the welded material, the lower strength in case of face-to-face welding can be explained by the low mechanical properties of the surface layer of the wood-based panels.

14.3.5 Perspectives

The linear welding technology is a very promising assembling process with a huge potential in the wood industry. The rapidity of the process and the good performances for interior application should motivate furniture producer to adopt in this technology.

14.4 Basic Press Systems

Pressing processes are indispensable in the processing of wood, in order to be able to produce joints in wooden constructions as well as dimensionally stable wooden composite materials. In addition, pressing processes are also used for surface coating with veneers, films, or other solid materials.

Goals of pressing processes can be:

- Producing a final product with certain final properties (density, strength, modulus of elasticity)
- Generating a shape and ageing resistant material
- Generation of certain surface properties
- Generation of certain shapes and geometries
- Good processability of the composite material

In terms of production technology, pressing is assigned to joining or forming, and in some cases to changing material properties. There, a change in the shape (in most cases thickness of the composite material) and/or the surface texture on the workpiece occurs. The mass of the material system is retained, apart from mass changes due to chemical reactions and changes in the moisture content of the material and in lesser extent due to evaporation of volatile compounds or degradation products. The cohesion of the raw material is either increased or at least remains the same. In many cases, there is a general or local increase in the bulk density of the material composite with the formation of a special density profile (for example, particleboard and fiberboard production). When pressing on surface coating materials or when joining of components, there is usually no forming but only a joining, except of special so-called compacted veneer lumber or high density plywood.

The application of an energy potential is crucial in the pressing process, which can be fundamentally described by the pressing pressure. The joining, forming, or material properties change take place due to external forces and moments.

General information on the pressing process and the associated technology for the production and coating of wood-based materials and components can be found in the publications of Thoemen et al. [560], Paulitsch and Barbu

[561], Dunky and Niemz [562], Pankoke [563], Rowell [564], Pizzi [565], as well as Wagenführ and Scholz [566] among others.

14.4.1 Fundamentals of Pressing

When pressing material systems into composite materials, when coating materials or when joining components, various combined processes take place. In addition to the external mechanical pressure (compaction process), there is often thermal heating or cooling (mass and heat transfer) and, if necessary, setting of a binder used (effect of the binding force). A number of process parameters play an important role in such processes. In the following, these processes and parameters for various forming and joining applications (pressing of particulate mats (fiber or particles), joining of veneer layers or solid wood elements, forming of moldings, coatings, joining of wood joints, frames, and cabinets) will be in the focus of description.

Important Parameters of Pressing

The **pressing time** (s) indicates the duration of the action of a pressure potential in the press. Very often this time is related to the final thickness of the board material to be generated and referred to as **specific pressing time factor** (s/mm). The pressing time usually includes the so-called **heat-up time** (s), also expressed sometimes by the **heat-up rate** (mm/s), which describes the complete heating of the material cross-section, which is to be pressed. For some applications (particle composite material production), also the **speed to close the press** (mm/s) as well as the time span to reach the target thickness (s) is important for the pressing process with respect to the formation of a specific density profile.

The **pressing temperature** (°C) describes the temperature in the contact zone (pressing area) between the press platens and the surface of the material to be pressed (see Fig. 14.35). Pressing temperature and pressing time influence the bonding time of the binder as well as the necessary heat-up speed of the pressed material during pressing. There is a fundamental distinction between

- Cold pressing (18–23 °C, long pressing times, for pressing of inorganic bonded composite materials or glulam)
- Warm pressing (60–90 °C, medium pressing times, pre-pressing)
- Hot pressing I (100–140 °C, moderate pressing times, pressing of plywood)
- Hot pressing II (180–230 °C, short pressing times – 3–12 s/mm of board thickness, for particle or fiber particle- or fiber-composite materials depending on board type and on press type)

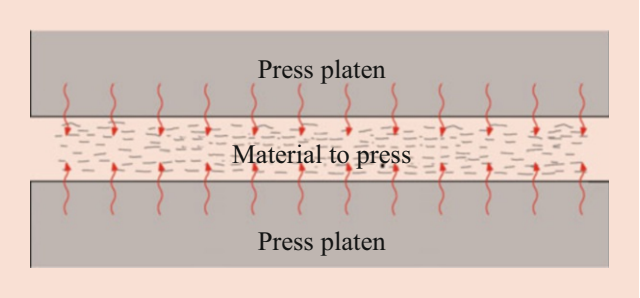

Fig. 14.35 Heat transfer from the press platens (contact area) into the pressed material. In some cases, there is also the possibility of a re-cooling of the pressed material by a negative heat flow (heat removal)

In addition to contact heating, other modes of heat energy transfer (convection, radiation, high frequency) to the pressed material are possible. Eq. 14.1 describes the heat transfer rate dQ/dt.

$$\dot{Q} = \frac{dQ}{dt} = \frac{A \cdot \Delta T}{\left(\frac{1}{\alpha} + \frac{\delta}{\lambda}\right)} + h \cdot \dot{m} \qquad (14.1)$$

whereas

- ΔT ... Temperature difference between heating platen and the middle (core) of material to be pressed (e.g., particulate mat)
- α... Heat transfer coefficient
- δ ... Half thickness of the material to be pressed
- A ... Press platen area
- λ ... Coefficient of thermal conductivity
- $h = c * T$ ... Specific enthalpy
- c ... Specific heat capacity
- $\dot{m}$ ... Vapor flow
- $1/\alpha$ ... Heat transfer heating platen to the material to be pressed
- δ/λ ... Heat conduction within the material to be pressed
- $h * m$ (dot) ... Convection

The **pressing pressure** (MPa) describes the forming potential. Since the counterpressure in the pressed material often changes during the pressing period, the pressing pressure usually changes with time. This can be represented by the so-called pressure diagram which shows the pressure depending on the pressing time. If the pressure remains the same during the forming process, it is called an **isobaric pressure** curve. If the volume of material to be compacted is kept constantly during forming or joining (for example, in

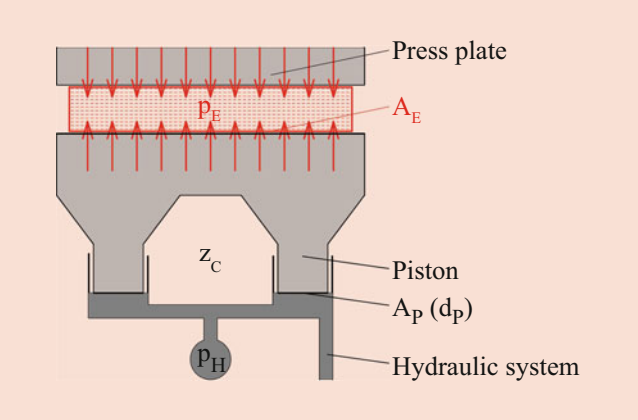

Fig. 14.36 Schematic representation of a hydraulic press (flat press)

the case of a thickness control), this is referred to as an **isochoric pressure** curve.

In the case of flat pressing processes, the pressing pressure, ultimately acting in the material to be processed, depends on the area occupied by the material between the press platens or the press bands and the fluid pressure present in the hydraulic system [14.8]. This hydraulic pressure is visualized by the hydraulic pressure display on the press and acts against the pistons in the press cylinders during the pressing process in Fig. 14.36. The conversion of this **hydraulic pressure p_H** into the **effective pressing pressure p_E** can be done with Eq. 14.2:

$$p_E = \frac{\pi \cdot d_p^2 \cdot z_C \cdot p_H \cdot \eta}{4 \cdot A_E} \qquad (14.2)$$

whereas

- d_P ... Piston diameter
- z_C ... Number of press cylinders
- p_H ... Hydraulic pressure
- A_E ... Used pressing area
- η ... Overall system efficiency (0.835–0.995)

Pressing of Particulate Mats

When pressing primary shaped particulate mats (fibers or particles), mats with low bulk density (about 30–250 g/m^3) and high bulk resilience behavior are compressed to high densities of about 500–850 kg/m^3 and higher. In this case, the thickness of the particulate mat decreases approximately with the factor 5–15.

First, a pre-compaction of the particulate mat takes place, in order

- To reduce the height of the mat (reduction of opening width of the press, press path, press closing time)
- To overcome the bulkiness
- To achieve a better manipulability
- To reduce the sensitivity of the particulate mat (strength increase), as well as
- If necessary, to achieve a pre-dewatering of the mat (wet process)

Pre-press systems can be opening presses, continuous calendar roll presses, or band presses (Fig. 14.37). The pressing pressure is in a range between 1 MPa and 3.5 MPa [566].

The cold pressing process uses a compression pressure between 0.4 MPa and 4 MPa. There is only a slight increase in the cohesion of the particulate mat and density up to about 200 kg/m^3. The pressure effects only for a short time and then it comes to a springback of the particulate mat.

However, preheating (microwave or high frequency) of the mat at about 50–80 °C can also be coupled to the pre-pressing. This leads to a reduction of the pressing time and general to process acceleration.

If necessary, a mat formatting process (circular saws) is also carried out to minimize the subsequent panel oversize and the associated material losses. In addition, the excess particle material can be returned to the pre-staged scattering process before the hot pressing process. This also avoids excess cured panel material and thus hazardous waste.

Then the manipulation of the pre-compressed particulate mat to the main press takes place, wherein the particle structures within the particulate mat may not be destroyed.

In the main pressing process, in addition to the densification of the mat, heat transfer is the first priority in order to activate the adhesive and to accelerate the binding process by a rapid and uniform heating of the particulate mat. It forms a temperature gradient over the cross-section of the mat. The heat passes from the contact surface of the press towards the middle (core) of the particulate mat. The press temperatures for particle composite materials are usually in a range up to 230 °C (150–200 °C).

There is a risk of premature curing of the outer zones of the composite board (edge zone compaction). Therefore, buffer solutions or a lower proportion of hardener in the adhesive mix are used for adhesive coating of the outer layer's particles in the mat (reduction of the reactivity). Also, a quick closing of the press can be helpful to keep the temperature gradient low.

Due to the moisture content of the adhesive-coated lignocellulosic particles in the mat, the heat transfer process also leads to a moisture gradient in the mat cross-section. In the process, the particle moisture changes to the gaseous state, which results in an increase in the local vapor pressure. Therefore, the resulting water vapor leads to a steam jet (pressure gradient) which is directed from the particulate mat surface (pressing area) into the inner layers of the mat. The mass transfer process of the water vapor through the mat

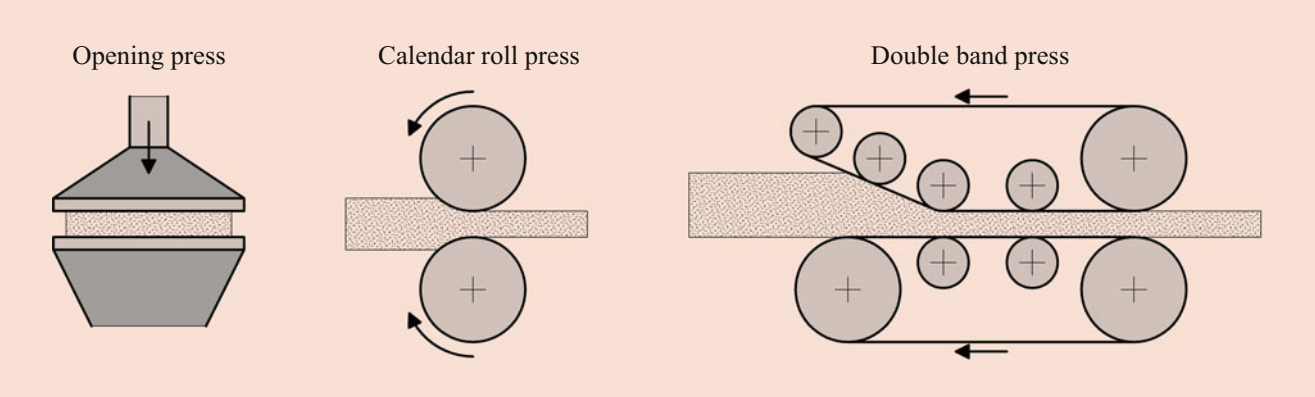

Fig. 14.37 Pre-press systems

causes a faster heating of the particulate mat (vapor diffusion) and binder activation. Finally, in the core layer of the particulate mat, there is a gradient reversal of vapor pressure and a danger of local steam nests. These can become wide cracks within the core layer parallel to the board plane destroying the panel when leaving the press. The risk of this cracks increases with elevated density of the particle composite material. To avoid this cracking phenomenon, a short-term release of the particulate mat must take place immediately after the action of the steam jet, for example, by a short pressure reduction of the hot press.

The described steam effect can be deliberately brought about by a moisture gradient ($\Delta\omega$) between the outer and the core layers of the particulate mat:

- $\omega_{\text{outer layer}} > \omega_{\text{core layer}}$
- Application of moisture to the mat surfaces (about 10–30 g H_2O/m^2 for particleboard and 20–50 g H_2O/m^2 for MDF – all numbers single side addition)
- Higher water content in the adhesive for adhesive coating the outer layer particles (dilution)

Thus, an accelerated heating up of the core layer of the particulate mat and, hence, pressing time reduction as well as through hardening of the adhesive are possible.

There is a pressure gradient in the cross-section of the particulate mat, which is obtained due to the saturated steam development with the steam effect and due to reaction gases of the binder. At the edge of the board (narrow surfaces of the resulting board material), the vapor pressure drops, because the steam can escape there. The densification of the face layers (outer layer) comes from the fact that at the start of the press cycle mainly the face layer is densified by heat and steam, whereas the core layer is still "relatively cold" and therefore more difficult to densify. Core layer densification then only occurs when enough heat has reached the core.

The general compaction process and bonding of the particulate mat towards the finished particleboard or fiberboard can be described by a reduction of elastic springback energy and the setting of a permanent change in shape. The timing of the compaction of the particulate mat is crucial for the formation of the bulk density profile over the composite material cross-section. A simplistic modeling of the conditions can be performed by using of spring and damper links taking different layers of the particulate mat into account (Fig. 14.38). The spring links stand for the springback behavior in the particulate mat layers, the damper links symbolize the increasing effect of the binder and the transverse tensile strength in the composite material layer and the blocking of the springback.

The achievement of a sufficient bonding strength in the particulate mat is possible only at a sufficiently high counterpressure within the mat. The highest counterforce comes from the particles of the core layer (for example, hard, coarse particles) with an inhomogeneous mat structure. However, heat and moisture reduce the counterpressure in the particulate mat due to the onset of plasticization of the lignocellulosic particles and the binder loses viscosity. This reduces the friction between the particles.

The setting of the binder ultimately leads to an increase in adhesive forces, which better counteract the elastic restoring forces within the particulate mat. It comes to a stress relaxation and fixation of the composite. The condition for the completion of the pressing process is that the transverse tensile strength in the particulate mat cross-section must be higher than the prevailing internal pressure in the particles or in the resulting board (Fig. 14.39).

The pressure of the press must generally be secured higher than the internal pressure in the particulate mat. In former times this was achieved by generating an overpressure and using spacer bars between the press plates. Today, however, modern presses work with a distance control in which the closing or opening movement of the press can be preselected in accordance with a distance diagram (pressing path diagram). Then the control system holds the desired thickness of

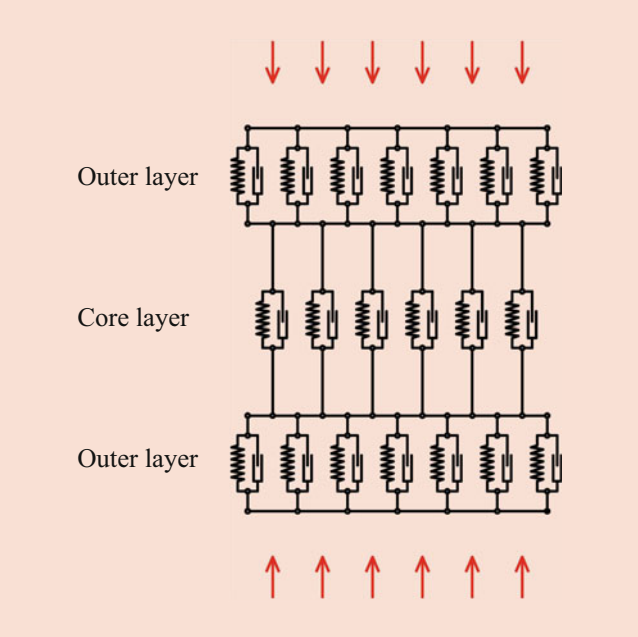

Fig. 14.38 Model of forming a particulate mat with spring and damper links in different layers

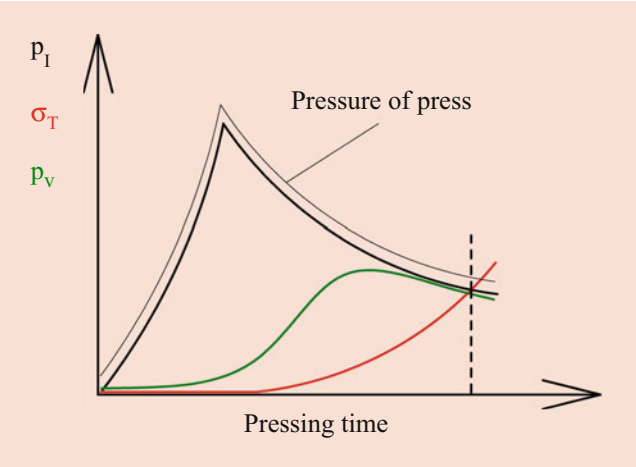

Fig. 14.39 Development of the pressing pressure, the internal pressure p_I, the vapor pressure p_V, and the transverse tensile strength σ_T in the particulate mat cross-section

the particulate mat respectively the board during the pressing. In this case, the currently required pressure of the press is permanently adjusted to the distance control. This is also a way to minimize the energy requirements.

Finally, the post-processing of the formed particle composite material includes a trimming with circular saws (longitudinal trimming and transverse cutting). The board dimensions and clean narrow surfaces and edges are generated. In addition, there is a partly cooling of the composite material boards in a star cooler (all-round air circulation). There, a defined cooling of the hot composite material take place to prevent a heat accumulation in the board or board stacks. Otherwise it can lead to a loss of strength due to binder hydrolysis (which mainly is a certain risk with UF resin).

The subsequent sanding of the raw boards with multistage, double-sided wide-belt sanders is used to level out unevenness and to calibration the thickness of the boards. This leads to a removal of the press skin, a burn-off and scale layer, which would be negative for the coatability of the boards.

Sorting and storage of the particle composite boards completes the post-processing and curing process.

Joining of Veneer Layers

Laminated wood, such as laminated veneer lumber (LVL) or plywood, is produced by joining of veneer layers coated with adhesive. The joining process begins by stacking the coated veneer layers one above the other. For laminated veneer lumber, a layer alignment of the grain parallel to the long dimension of the lumber is used for every veneer layer in the composite material. In the case of plywood, the layers are rotated by 90° regarding the grain orientation from one layer to the next. Laminated veneer lumber can be formed by endless formation through partial overlapping, finger jointing or scarf jointing of the veneers, or by cascading (staircase-like arrangement) in which the veneers are laid overlapping from one layer to another.

The subsequent forming process (pressing) then takes place on single- or multi-opening presses (plywood) or on continuous double band presses (LVL). Moldings (molded plywood) are hot-pressed on molding presses with specially optimized dies. Cold pre-pressing of laminated wood is also possible.

The main pressing process (plywood) can be done with the forming parameters according to Table 14.2. The pressing conditions must allow an adhesive hardening. Adhesive films or usually liquid adhesives are used for laminated veneer wood composites. For compacted veneer lumber, higher compression pressures than the compressive strength of the veneer (wood) in the range between 2.5 MPa and 8.0 MPa are required. The pressing time depends on the adhesive type and the board thickness.

After pressing, the treatment of the laminated veneer wood involves conditioning with multiday deposition to cool down the composite, complete adhesive cure and moisture balancing. Finally, a formatting cut (circular saws) and a machining of the wide faces (belt sanding machine) are carried out before the storage of the composite material.

Joining of Solid-Wood Elements

Wood lamellae for glulam or solid wood panels are often longitudinally joined by finger jointing. These single segments of lumber are converted into an endless lamella. The joining process takes place in special continuous presses (hot

Table 14.2 Forming parameters when pressing plywood

Wood species	Softwoods	Hardwoods
Specific pressure	0.8–1.2 MPa	1.2–1.8 MPa
Type of adhesive	Aminoplastic resin (UF, MUF)	Phenolic resin (PF)
Press temperature	90–110 °C	135–165 °C

finger-jointing press). Then the wide and the longitudinal narrow faces of the endless lamella are milled and finally the material is cut to desired lengths (chop saw).

The surfaces of the lamellae parallel to the wood grain are usually side-jointed (side-bonding). The formatted lamellae are adhesive coated and folded together and finally cold-pressed as slat packages. This is done in hydraulic or mechanical vertical, horizontal or molding presses operating at room temperature. The pressing time is therefore about 4–8 h.

There are also hydraulic or mechanical block presses. These presses are heated by:

- Warm water (up to 80 °C)
- Hot water (up to 120 °C)
- Thermal oil (up to 150 °C)
- High frequency (with 15–120 kW)

Here, the pressing time is about 3–12 min. But there are also simple unheated block presses.

The joining of thickness-calibrated solid wood layers, for example, in solid wood panel production, takes place on multi-opening or 3D presses with membrane at a pressure of 0.4–1.0 MPa. The resulting composite element must be machined by planing or sanding (equalization of the glue joint surfaces, constructive processing).

Forming of Moldings

Molded wood composite parts can be produced as a particle composite material or as laminated veneer composite material (plywood moldings with grain direction of the veneer layers either all parallel or in plywood mode (90° from one to the other) or in mixed mode) among others.

For *molded parts as a particle composite material*, there is the possibility of material structure formation before the forming process in a molding pre-press at room temperature. For this purpose, the adhesive-coated particles can be defined scattered in the die (direct mat formation) and pre-pressed, with high requirements concerning the cold tack behavior of the resin and the stability of the pre-pressed parts before transferring them into the hot press. Another possibility is to prefabricate a flat particulate mat analogous to the production of flat particle composite material for the subsequent insertion of this mat in a molding press (external mat formation).

Generally, the particulate mat for molded parts is finally formed by a hot pressing process in special molding presses. The process is comparable to the hot pressing of flat particulate mats. Often solid coating films (melamine impregnated papers) are already inserted into the press die with the mat in order to achieve a surface coating (face) at the same time during the forming process. As a special feature, however, for forming processes without direct coating, the narrow surface (edge) of the particulate mat can be closed here. Thus, the internal pressure (vapor pressure) inside the mat is the same everywhere. The dissipation of the hot steam happens by channels in the press die. Partial re-cooling of the molding takes place before the press opening.

The treatment after the pressing of the particle-based molded parts consists of a conditioning and formatting.

In the case of *plywood moldings*, the adhesive-coated veneer layers are first combined in a defined manner concerning sequence of grain direction. The resulting veneer layer stack is then formed in a hot press analogous to flat plywood boards pressing. A general difference, however, is the use of a special pressing die. According to the desired molding design, there are presses with one or two press levels (horizontal or horizontal and vertical). Generally, the goal of the forming process is to avoid wrinkling and cracking in the veneers during forming.

After the removal of the molded product from the hot press, it is often clamped in a similar press die during the cooling period to avoid demolding of the composite material until the complete dimensional stability is obtained. The treatment after the pressing of the plywood molding also consists of conditioning and format processing.

Coatings

Solid coating materials, such as papers impregnated with melamine/urea resins for single-layer films and surface impregnation as well as phenolic resins for core layers (DPL/MFB – direct pressed laminates/melamine-faced board, HPL – high-pressure laminates, CPL – continuous pressure laminates), electron beam cured laminate coatings (ELESGO process), thermoplastic films (e.g., PVC), thermosetting films (decorative finish films), and veneers, can be applied to different substrates, such as particleboard, fiberboards, or plywood. For this, pressing processes are necessary. The laminating technology, 3D coating, lining and edge banding are used. Depending on the structure, adhesive, and application technology, the coating material is applied by cold or hot pressing in short-cycle opening presses, calendar roll presses, and 3D presses with or without a membrane [568].

Joining of Wood Joints, Frames, and Cabinets

The joining of wood joints or of frame and corpus constructions is achieved by applying adhesive to the joining surfaces and subsequent mating of the usually form-fitting connection parts. Thereafter, for example, in a frame or case press, the

exact angular form of the construction is ensured. The pressing pressure must be secured smaller than the relevant material strengths, so that there is no permanent deformation of the wooden structure [568].

14.4.2 Press Systems and Applications

Press systems can be fundamentally divided into discontinuous cycle (batch) presses and continuous presses. Another system for systemizing is the used material:

- Presses for the production of wood composite materials
- Presses for coating
- Presses for the assembly of components (frame and case presses)

Discontinuous Systems

Discontinuous presses (batch presses, cycle or opening presses) work in a certain time cycle. The cycles or clock consists of the following steps:

- Loading the press
- Closing the press
- Holding the pressing pressure according to the pressure diagram
- Opening the press
- Removal (unloading) of the pressed material (and in most cases, simultaneous loading of the press)

Cycle presses can be single- or multi-opening presses.

Single-opening presses are flat or molding presses in which only one element (particulate mat, laminate, etc.) or several elements, distributed over the pressing area, can be compressed, formed, or coated per cycle.

Multi-opening presses are in most cases flat presses, but also pressing of molded (3D) door skins is possible. According to the number of levels, several elements (particulate mats, laminates, etc.) can be compressed, formed, or coated per cycle.

Single-Opening Presses

Single-opening presses (single-daylight presses) are usually hydraulic top-piston presses (see Fig. 14.40). They offer a high accuracy, since only one press level and a static lower table are available. Today, they are mainly used for coating purposes and for molded composite parts manufacturing. But in rare cases (e.g., research laboratories), there is still also an application for particle or fiber composite material production.

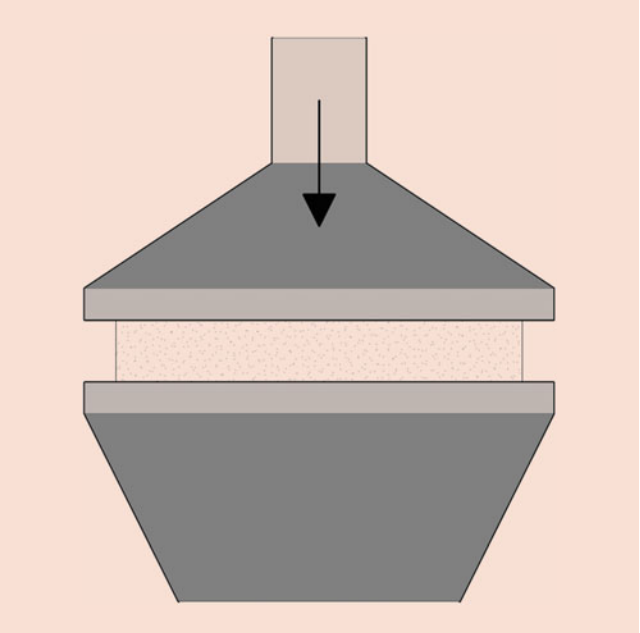

Fig. 14.40 Single-opening press

(a) For a former use in *particle or fiber composite material production*, high capacities are achieved only with a large pressing area (up to 60 m × 2.65 m), high input and output speeds of the particulate mat (up to 200 m/min), and a heated pre-pressing process. Press temperatures up to approx. 220 °C are selected. The specific pressing time at this temperature is usually for:
- Aminoplastic bonding (UF, MUF): 7–8.5 s/mm
- Phenolic bonding (PF): 9–11 s/mm
- Isocyanate bonding (pMDI): 7–8.5 s/mm

Systems (discontinuous or continuous) for scattering the particles to mats are used before the pressing process can start. This process must be synchronized with the clock cycle of the press. Also steam technology (steam injection presses) can be used in single-opening presses. In this case, small openings are provided in the press plates for a steam injection or vacuum extraction. Thus, a faster heating of just mats for thick composite material boards (from 40 mm) and thus short pressing time factors of about 1.5–2 s/mm are achieved.

Single-opening presses can also be re-cooled if necessary. However, there is a loss of capacity then [564, 566]

(b) For *coating purposes of board materials,* single-opening short-cycle presses are used. These presses work with an isochore characteristic and short press cycles.

For coatings with veneer, compression pressures in the range of 0.3–0.6 MPa and pressing temperatures of about 90–140 °C are selected. For melamine resin film coatings, compression pressures in the range of 2.5–4.0 MPa and press temperatures up to about 240 °C are set. The

effective length of the press for coating processes is up to approx. 13 m. Up to three pressing cycles per minute are possible. Thick heating plates and pressure distributing press pads with good heat transfer are used [569].

Multi-opening Presses

Multi-opening presses (multidaylight presses) are mostly hydraulic presses in which the piston moves the press plates up from the bottom (see Fig. 14.41). Due to the design and the closing mechanism for several press levels, they are less accurate. This is the reason for relatively large thickness tolerances when forming composite materials with this kind of press. Therefore, these presses are mainly no longer used for particleboard and fiberboard (MDF) production.

(a) Multi-opening presses with 25 or more press levels are used for *hardboard, laminated veneer lumber, and plywood production*. To achieve a uniform closing of all press levels, a mechanical simultaneous closing mechanism is attached to these presses. Thus, it ensures nearly the same technological conditions in every press level. To load and unload the press, special racks are required to allow a short cycle time.
High capacities are achieved on a relatively small pressing area ((2.5 m–12.0 m) × (1.5 m–2.65 m)). Press temperatures of up to 180 °C are selected. The specific pressing time at this temperature is usually for:
- Aminoplastic bonding (UF, MUF): 11–13 s/mm
- Phenolic bonding (PF): 12–13 s/mm
- Isocyanate bonding (PMDI): 11–12 s/mm

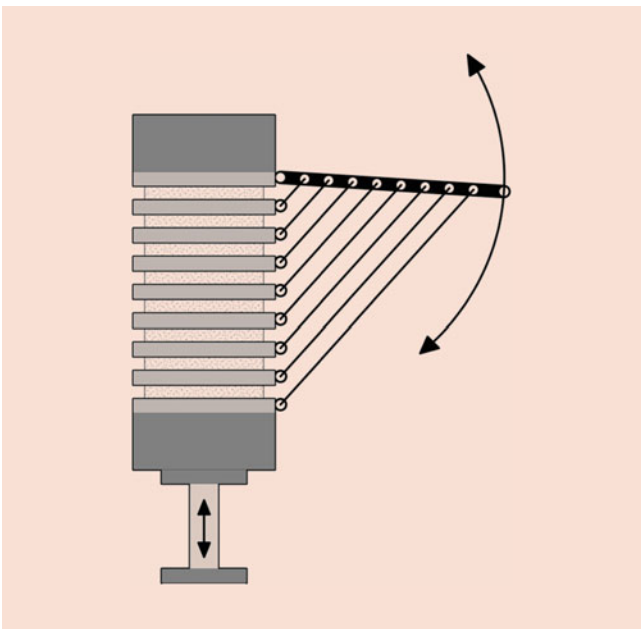

Fig. 14.41 Multi-opening press with mechanical simultaneous closing mechanism

Multi-opening presses are easy to control and very robust. A re-cooling with capacity loss is possible. Due to the limited opening height of the press, a strong pre-compaction of the particulate mat or the material to be pressed is necessary. A quick change-over to a new product batch is possible easily [564, 566]

(b) Multi-opening presses are also used for *coating of barrier doors and floor elements*, in part also for *coating of panels and building components with veneer*. They offer a high volume performance in a small space but with longer pressing times.
There are several types of these presses:
- Two separately operating presses on top of each other in a common cycle with external hydraulics and low overall height
- Several presses next to each other in common cycle (also on carousel)
- Height positioning press body with a counter-hydraulic in the manner of an elevator in a fixed frame, which always opens only one press level
- Two separate single presses on top of each other with press plates transversely divided into four sections each, which are controlled in accordance with all three workpiece dimensions with individually specified pressing pressure
- Star presses (rarely for barrier doors) – several single- or double-opening presses rotating vertically around a common axis (merry-go-round press) [569]

Block Presses (Stack Press)

Block presses are used for cold or hot *coating of boards or components* with films or decorative high-pressure laminates as well as in *plywood production in a stack*. This type of press is also used as a post-press behind continuous laminating equipment. If desired, there can be also a heating of the material to be pressed by means of high frequency. The retraction of the stacked material in the press happens via roller rails. If necessary, heating and compression of the material takes place then [569].

Molding Press

Molding presses are needed for the *production of molded parts as a particle composite material or made of veneer* (see Fig. 14.42). Special heated molding dies made of wood, aluminum, or steel are mounted on the flat press plates of a single-opening press. The heating can be done by high frequency, by steam, or by hot water. Depending on the complexity of the composite material to be formed, a combination of horizontal and vertical press dies (two different dimensional directions of press plate motions) are also sometimes used especially with veneer.

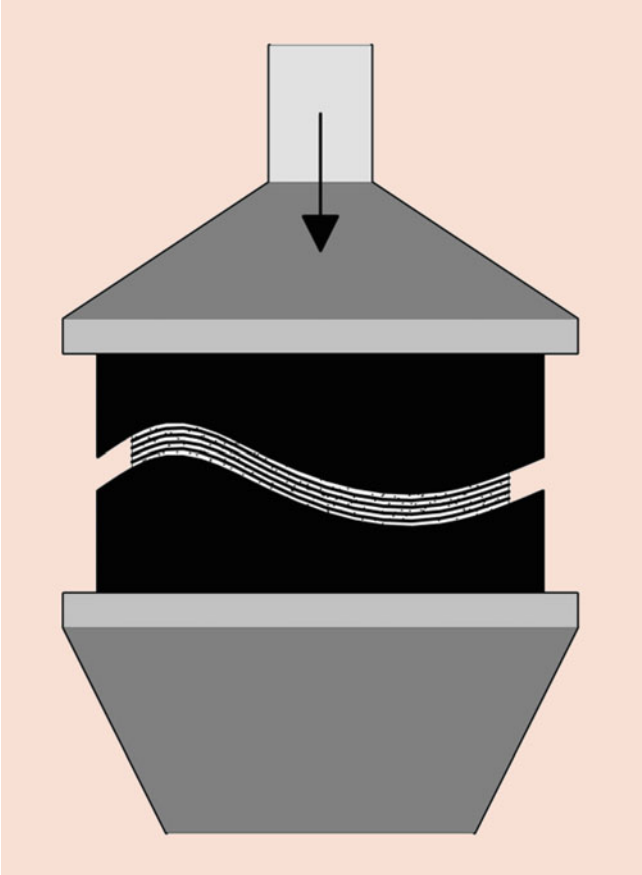

Fig. 14.42 Molding press

Presses for Coating Purposes

3D coating presses with or without membrane technology are used for efficient *3D coating of components* with internal or external profiles of the narrow faces (e.g., furniture fronts with deep cuts or round tabletops) with thermoplastic films or veneer.

(a) For *presses with a membrane*, it is possible to coat the component on both sides. From above, the membrane covers the workpiece deposited on a base socket in the press with the applied coating materials completely. When closing the press, air is evacuated from the space between the membrane and the coating. The vacuum causes a very high pressure, which acts evenly across the membrane and the covered material. Under certain circumstances, the membrane is preheated with the coating material prior to the pressing process and later heated from above by a stream of hot air during pressing

(b) Inside of *presses without a membrane* (see Fig. 14.43), heating of the coating material (foil) may first take place on an upper press plate (Fig. 14.43b). Thereafter, the tempered coating material is placed over the workpiece, which is resting on the lower press plate. Then the coating material is formed directly around the resting workpiece by hot compressed air (Fig. 14.43c). Thus, a coating of more distinctive profiles is possible. However, the heat potential of this press and the heat resistance of the adhesive joints are rather low

(c) For other *presses without a membrane*, a heating of the entire material to be pressed (substrate and coating) can take place. In this case, an incoming and outgoing acting infrared radiator panel is used to heat the substrate (workpiece) and the applied coating from both sides, above and below. After the press has been closed, hot compressed air is then fed for forming and the heat supply. Thus, the

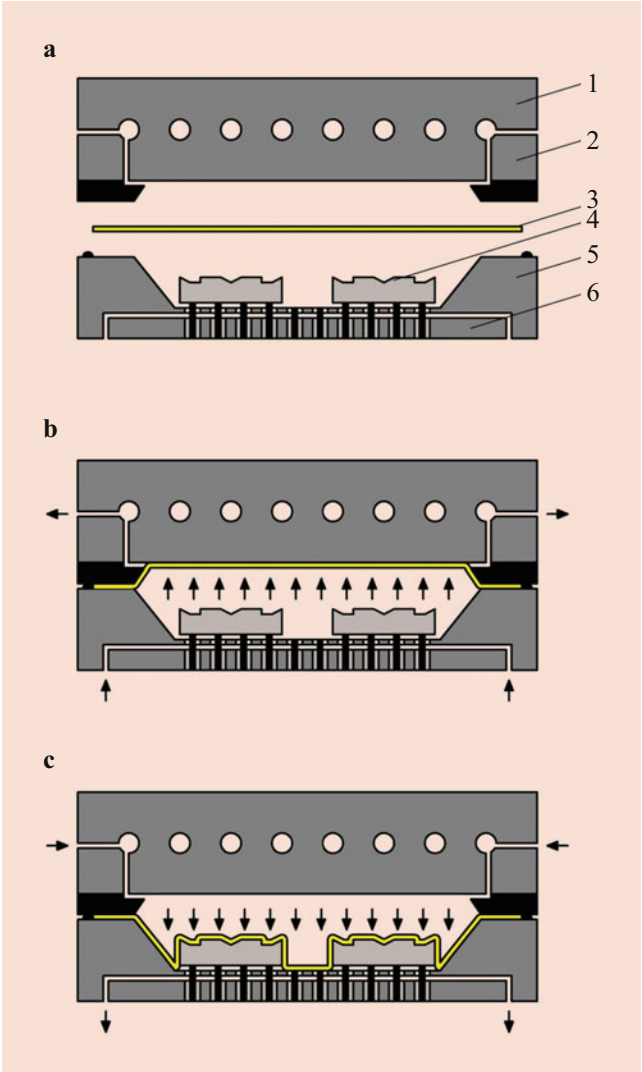

Fig. 14.43 3D coating press without a membrane (Bürkle company) – (**a**) Open press (1 – heating plate, 2 – upper seal frame, 3 – coating foil, 4 – part to be coated, 5 – laying pallet, 6 – bottom piece); (**b**) Coating foil is pressed with compressed air from below against the heating plate and heated; and (**c**) The warm foil is pulled over the parts by vacuum from below and pressed on with compressed air from above [566]

heat potential is better than in presses without membrane, in which only the coating material is heated (see section b). However, this leads to higher energy consumption

(d) In *waterbed presses*, a membrane rests on a hot waterbed. Here, first the coating material and then the workpiece is placed to be coated on the membrane. When the press is closed, a pressing area, acting from above, presses the substrate piece together with the coating material into the water-supported membrane. Thus, very high pressures without expensive process air and savings of coating material by fixed dimensions can be achieved. However, the tailoring of the coating material is very time-consuming, the work above the hot waterbed very stressful, and it is difficult to rationalize the exact placement of the material to be pressed on the waterbed [569]

Frame and Case Presses

Frame and case presses are used for precise angle joining and gluing of window frames, decorative frames, and other frame structures, as well as furniture baskets and other carcass structures. Various joining techniques such as bridle joint, dowel joint, biscuit joint, or folding joint are used. The presses consist of spatially arranged, linearly adjustable pressing jaws, which can be set by means of threaded spindles or hydraulically. During pressing process, a two-dimensional pressing of the resulting frame or carcass construction takes place (see Fig. 14.44).

Continuous Systems

Continuous presses work permanently with a certain feed rate in a production line. This speed determines the production flow. Due to the continuous mode of operation, a continuous production can be carried out with high freedom of format. Continuous presses are always one-floor presses.

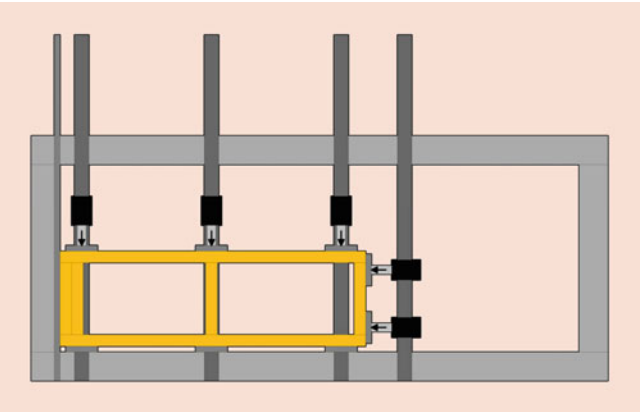

Fig. 14.44 Frame press

Double Band Presses

Continuous flat-bed double band presses (Fig. 14.45) have emerged from the 1950s presses with plate chains (Bartrev method). Since the 1970s, they are used for pre-pressing and since about 1985 as the main press in wood-based panel production. But also an application for coating tasks takes place.

(a) Double band presses are determinant today in the *production of fiberboard (MDF), particleboard, oriented strandboard (OSB), and laminated veneer lumber (LVL)*. They have a well controllable compression curve at the inlet through a tilt-adjustable press mouth. Overall, a specific pressure profile over the press length can be applied to the pressed material. For this purpose, a main hydraulic system with individually adjustable pressure cylinders acting from above along the press length is used. There is also a bottom-acting control hydraulic with individual pistons per yoke.
Overall, double band presses have prevailed in the wood-based material industry, as they are more energy-efficient and resource-efficient than discontinuous press systems. Low thickness tolerances also allow a direct coating of the pressed composite material.

The press works with static press plates and dynamic steel press bands. The heat is transferred from the heated press plates via the steel bands to the pressed material. The pressure transmission is realized via hydraulic cylinders which are coupled to the press plates. Again, this static plates are connected to the moving steel bands and thus to the particulate mat or staked veneers to be pressed. Here it is very important to minimize the friction between the press plates and the steel band. This is realized by a revolving roll bar carpet or a circulating lashing chain carpet without self-propulsion (ball-bearing principle) between press plates and steel press band. An isochoric, calibrated pressing characteristic is possible. Another less common variant to minimize the mentioned friction was the use of a hydrodynamic oil film according to the plain bearing principle between press plates and steel press band (Hydro-Dyn). Here, an

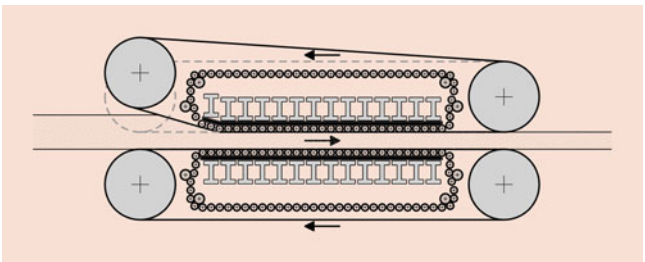

Fig. 14.45 Double band press

isobaric pressing characteristic is determining for the system. This type of system is no longer in use due to excess consumption of oil [569].

In double band presses, the pressing time is controlled by the feed speed and the press length. Depending on the application, the following press lengths are used:

- Standard – 38–45 m
- Chipboard – 45–62 m
- MDF – 35–50 m
- Thin MDF – 15–25 m
- OSB – 40–60 m [567]

(b) Double band presses are also used for the *production of decorative high-pressure laminate and for the direct coating of boards with aminoplastic films*. There are also different systems of pressure and heat transfer to fundamentally reduce friction in the system. On the one hand, with an isobaric pressure system as an air cushion or with free-flowing oil as the lubricant, the same pressing pressure is achieved across the pressing area. On the other hand, an isobaric band support can be obtained by rollers running in ball bearings

(c) *Pre-presses* are mostly double band presses today. They are used between particulate mat forming station and continuous hot press (see Fig. 14.37). Especially in MDF production, these presses are very important for a height reduction of the particulate mat to allow lower opening heights and hydraulic paths of the main press. These continuous pre-presses are heavy band presses, which form a conical compaction gap at the inlet [563, 564, 566, 568].

Mende (Rotocure) Presses

Since 1971, the so-called Mende process (Bison Company) is used for the *production of thin MDF and particleboard* from 2 mm to about 12 mm. It was the first continuous process for commercial thin particleboard production. The scattered particulate mat is continuously transported on a steel band to a heated calendar roll (diameter 3–5 m). The steel band wraps around the large roll. This compacts the particulate mat between the steel band and the calendar roll during the run around the roll. During this process, a system of pressure rollers (calibrating rollers with additional heat input) acts against the steel band and the pressed material from the outside against the calendar.

The system consists of three stages:

- Pre-press
- In case (but rather seldom) high frequency preheating of the particulate mat
- Calendar press

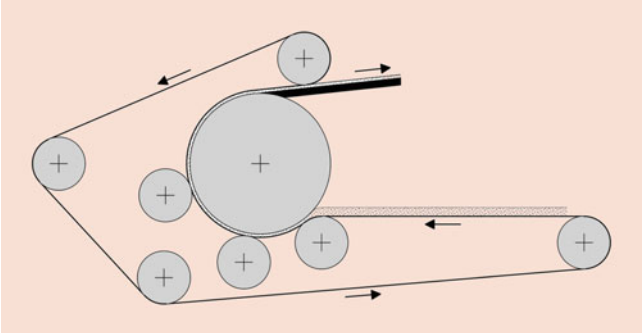

Fig. 14.46 Mende press

The feed rate in the production line is selected between 5 m/min and 18 m/min and more. The pressing time results from the roll diameter, the roll rotation speed, and the wrapping angle of the steel band around the calendar roll (Fig. 14.46) [563, 566, 569].

Calendar Roll Presses

(a) Double-sided calendar roll presses are used for *continuous pre-pressing of particulate mats and hot lamination of wood-based panels with roll-type coating agents* (Fig. 14.47a and b). Hard steel rollers generate a line pressure on the substrate board material from above and from below. The specific pressure and the pressing time are indefinite. Depending on the roll diameter and the elastic compression of the substrate, the line pressure (line load) becomes a pressure on an area. Thus, an ironing effect on the surface of the material to be pressed effects at high pressure. Due to the short pressing time, a coordinated pre-drying of the applied adhesive and preheating of the substrate board material is expedient

(b) The principle of a single-sided calendar roll press is applied to the *edge banding process on wood particle composite boards* like furniture components (Fig. 14.47c). The coating of the narrow faces of the board material with wooden or plastic edge bands takes place by using a hot melt-bonding process. The adhesive-activated coating band is pressed by a main-roll and following small sub-rolls against the moved substrate board its narrow face [563, 566, 568, 569]

Extrusion Press

The extrusion process is the oldest continuous pressing process for the production of wood particle composite materials and was patented in 1949 as Okal process by Otto Kreibaum from Lauenstein, Germany. At the center of the process is a simply clocked isochoric tamping press (see Fig. 14.48). Quasi-continuously, adhesive-coated wood chips are added and tamped cyclically into a forming shaft by an extrusion die and a periodical compression of the material takes place. The forming shaft has a constant cross-section, in which also

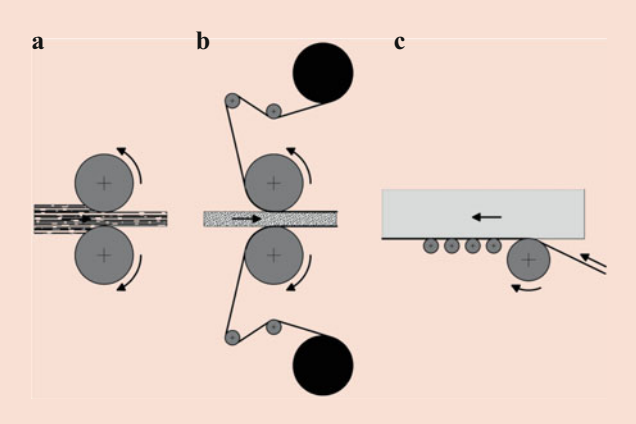

Fig. 14.47 Calendar roll presses – (**a**) double-sided pre-press for particulate mats, (**b**) double-sided press for hot lamination of boards, (**c**) single-sided press for edge banding of boards

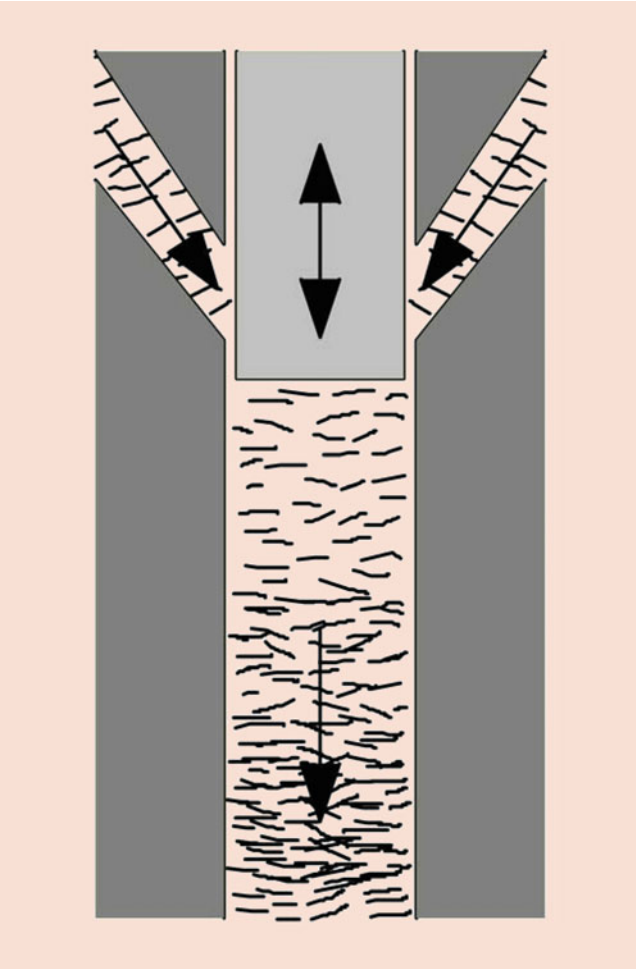

Fig. 14.48 Extrusion press

mounted tubes with circulation heating for heat input into the pressed material can be located. In this case, particleboard with certain tubes is obtained after the forming. The basic principle of the process is similar to piston extrusion. The feed rate of the extrusion line is between 0.8 m/min and 1.2 m/min.

In contrast to particleboard pressed by a flat opening press, the chips are oriented transversely to the plane of the board during the extrusion process (low bending strength, high transverse tensile strength). Extruded particleboard is used almost exclusively for door core layers [563, 566, 569].

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