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Transcrystalline interphases in natural fiber-PP composites: effect of coupling agent

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Abstract– The interest in lignocellulosic fiber composites has been growing in recent years because of their high specific properties. In this work, a new technique was used to prepare specimen to observe the transcrystalline zones in kenaf fiber–polypropylene composites. A maleated polypropylene (MAPP) coupling agent was used to improve the stress-transfer efficiency in the composites. Transcrystallinity was observed for both the uncoupled and coupled composites, although the rate of growth was higher for the coupled composites. Dynamic mechanical spectroscopy was used to observe the relaxations of the composites. The peak temperature of the β-relaxation, associated with the glass–rubber transition of the amorphous molecules, of the coupled composites was higher than that of the uncoupled composites. Restricted molecular mobility due to covalent interactions between the MAPP and the lignocellulosic surface may account for the shift to higher temperatures. It appears that during compounding the extractives sheared from the fiber surface is an important factor in determining the β-relaxation of these composites. The intensities of the a-transition, related to molecular mobility associated with the presence of crystals, is proportional to the fiber volume fraction. Thus it is possible that the molecules responsible for the a-transition are predominantly in the transcrystalline zone. These 'rigid' amorphous molecules in the transcrystalline zone do play a role in composite behavior and need to be considered when tailoring interphases.

Keywords: Transcrystallinity; kenaf fiber; natural fiber composites; fiber-reinforced PP composite; dynamic mechanical analysis; coupling agents.

1. INTRODUCTION

Kenaf fibers are extracted from the bast of the plant Hibiscus cannabinus and filament lengths longer than 1 m are common. These filaments consist of discrete individual fibers, generally 2 mm to 6 mm long, which are, themselves, composites of predominantly cellulose, lignin and hemicelluloses. Filament and individual

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fiber properties can vary depending on the source, age, separating techniques, and history of the fiber. Furthermore, the properties of the fibers are difficult to measure and we have made no attempt to measure the properties of individual kenaf fibers. The choice of the fiber for plastics applications depends on the availability of the fiber in the region, and also on the ultimate composite properties needed for the specific application. Kenaf was chosen for the study because it is now a fiber crop grown commercially in the United States. Several other fibers isolated from annual growth crops have potential as reinforcing fillers in plastics. The specific moduli of kenaf polypropylene composites are comparable to those of glass polypropylene composites and have potential in the automotive, building and furniture industries. More details of the mechanical properties of kenaf composites can be found elsewhere [1, 2].

The quality and type of natural fibers affect the reinforcing efficiency of the composites. Natural lignocellulosic fibers are themselves composites that consist of a framework of crystalline cellulose in a matrix consisting mainly of lignin and polysaccharides. Several other components such as inorganic salts, waxes, etc. are also present in smaller quantities. The properties of the fibers are thus dependent on the characteristics, amount and orientation of the reinforcing element, which is the crystalline cellulose. The degree of polymerization of the crystalline cellulose is an important factor that influences fiber strength and modulus. The fiber history includes the species, growing conditions, climatic and soil conditions that can also influence the properties of the fiber. An interesting example is that a species of flax fibers that grow in the summer months in Iceland have very good Young's moduli and strengths. This has been attributed to an unusually high degree of polymerization of the crystalline cellulose, possibly due to the long hours of daylight in the region [3].

Recent work indicates defects dominate the final strength properties of the fibers. There is little one can do about the inherent defects in the fibers. However, major defects are introduced during the fiber separation procedure. Recent work in a laboratory scale operation [4, 5] using controlled separation of bast fibers using enzymes indicate a significant reduction in the amount of defects in the fiber. Strengths of flax fibers, separated to give short fibers with high aspect ratios, could well be over 1.5 GPa. The real challenge is to have a commercially viable technique to separate these fibers.

In semi-crystalline polymers, the type and the amounts of the amorphous and crystalline phases govern the linear viscoelastic response during dynamic loading. Furthermore, the presence of fillers/fibers in the polymer creates further complexities in the morphology of the system. The surface properties of filler/fibers, and the use of a coupling agent or/and other additives can alter the morphology of the bulk polymer phase and that of the interphase. This, in turn influences the mechanical and dynamic properties of the system.

The fiber–matrix interface and interphase are complex morphological subjects whose characteristics are governed by numerous factors such as chemical, physical,

mechanical and processing techniques [6, 7]. The deposition of long chain macromolecules onto a surface can result in properties of the interphasial region being quite different from the bulk phase [8]. Transcrystallinity developed on surfaces further complicates the mechanisms of stress transfer from the matrix to the fiber.

2. EXPERIMENTAL METHODS

2.1. Compounding and testing

Kenaf filaments, a few inches long, harvested from mature plants were obtained from Ken-Gro Corporation, Mississippi, and cut into lengths of about 1 cm. The fibers were not additionally dried to remove any of the moisture present, and the moisture content of the fibers varied from 5% to about 9% by weight. In all our experiments, the weight and volume percent reported is the amount of dry fiber present in the blend. The homopolymer was Fortilene-1602 (Solvay Polymers, TX) with a melt flow index of 12 g/10 min as measured by ASTM D-1238. A maleic anhydride grafted polypropylene (MAPP from Aristech #880) was used as a coupling agent (at 3% of total composite weight) to improve the compatibility and adhesion between the fibers and matrix.

The short fibers, MAPP and PP were compounded in a high intensity kinetic mixer where the only source of heat is generated through the kinetic energy of rotating blades. The blending was accomplished at 4600 rpm that resulted in a blade tip speed of about 30 m/s and then automatically discharged at 190°C. A total weight (fibers, PP and MAPP) of 150 g was used for each batch and about 1.5 kg of blended material was prepared for each set of experiments. The total residence time of the blending operation depended on the proportions of fiber and PP present and averaged about 2 min. The mixed blends were then granulated.

Prior to molding, the granules (thermokinetic mixer) or pellets were dried at 105°C for 4 h. Test specimen were injection molded at 190°C using a Cincinnati Milacron Molder and injection pressures varied from 2.75 MPa to 8.3 MPa depending on the constituents of the blend. Specimen dimensions were according to the respective ASTM standards.

The blended specimens were stored under controlled conditions for three days before testing. Tensile tests were conducted according to ASTM 638-90, Izod impact strength tests according to ASTM D 256-90, and flexural testing using the ASTM 790-90 standard. The crosshead speed during the tension and flexural testing was 5 mm/min. The experiments were designed around the weight percent of kenaf in the composites; fiber volume fractions can be estimated from composite density measurements and the weights of dry kenaf fibers and matrix in the composite. The density of the kenaf present in the composite was estimated to be 1.45 g/cc.

Dynamic properties of the composites were measured using a Rheometrics DMTA MKIII. The samples were cut to size from injection molding flexural samples and

efforts were made to get the sample from identical spots on samples. A single cantilever test was used for the testing with a span of 14 mm, and sample width and depth were about 5 mm and 1 mm, respectively. The deflection amplitude was 16 μm, frequency 1 Hz and the heating ramp rate was 2°C/min and strain about0.0001.

A Perkin Elmer DSC was used to evaluate the crystallization and melting behavior of some of the blends. The samples were first heated to 220°C at 20°C/min and then held isothermally for 1 min. The samples were then cooled at 10°C to collect crystallization data, and then heated again at 10°C to observe the melting transition. The sample sizes were kept between 9 to 11 mg and all tests were run under nitrogen gas.

2.2. Microscopy

In prior work, to observe transcrystallinity in coupled systems, model systems were used where the MAPP was first reacted with the fiber using a solvent [9]. The fibers were then placed between films of the polymer before proceeding with the hot stage microscopy. In this work, we have used a new 'solventless' technique to obtain thin films of fibers in polymer to be placed in a polarizing microscope with a hot stage. The fibers, PP and the MAPP (if used) were first blended in the thermokinetic mixer as previously described. The granulated blend was then diluted to about 1% by adding pure PP. Samples were injection molded at higher than typical pressures. This higher pressure resulted in 'flashing' in the molded specimen. The fibers in the 'flashed' film were well dispersed so individual fibers could be clearly observed. We did try using a 20% 'flashed' layer, but it was not possible to observe individual fibers. Both coupled and uncoupled blends were prepared. Since the MAPP reacts with the fibers during the compounding process, the fibers dispersed in the diluted 'flashed' samples already have the reacted surface layer. If necessary, the films were again pressed to thinner films so that the transcrystallinity could be observed. Samples were heated to 220°C to remove the polymer morphological history, and crystallization was conducted under isothermal conditions at 130°C. As soon as the transcrystalline zones were formed, the samples were quenched and photographed.

3. RESULTS AND DISCUSSION

The interphase characteristics influence the mechanical and physical behavior of natural fiber/polypropylene composites. Details of the physical state such as whether the composite is above or below the glass transition and the nature and degree of crystallinity affect the stress transfer efficiency. Grafted polymers such as MAPP have been used to improve the mechanical properties of natural fiber composites [10]. Property enhancement can be significant and a two-fold increase (approximately) in tensile strengths of 50% by weight kenaf fiber filled PP have been reported with the addition of an appropriate MAPP [2].

The molecular weight and amount of grafted maleic anhydride of MAPP are important parameters in determining the effectiveness of stress transfer. Gatenholm *et al.* [11] have indicated covalent bonding of the grafted moiety to the hydroxyl group on the fiber surface through IR and ESCA analysis. Felix and Gatenholm [9] have suggested that brush-like interfaces exist while using the MAPP. This brush-like interphase for lignocellulosic–PP composites was postulated partly based on nucleation densities calculated from model systems observed under a polarizing microscope. These experiments were performed using a fiber placed in a PP melt. To observe coupling agent effects, the MAPP was first covalently bonded to the fibers using a solvent. The fibers were then dried and placed in a PP melt to be observed under a polarizing microscope.

Using the 'solventless' technique for the formation of thin films we observed transcrystalline zones for both the uncoupled (Fig. 1) and coupled systems (Fig. 2). It was observed that the crystallization rate was higher for the coupled system, although the rates of crystallization were not studied. The zone nucleated at several points on the fiber surface, and then grew radially outwards. Notice the concave outer edges of the transcrystalline zones suggesting radial growth (Figs 1 and 2). Neighboring crystals impinged on each other to limit the range of lateral growth.

The stress transfer efficiency of the composite is dependent on the properties of the interphase zone, and this includes the physical or chemical interactions between two different interfaces. The first is the interface between the transcrystalline zone and the fibers, and the second is the interface between the outer edges of transcrystalline

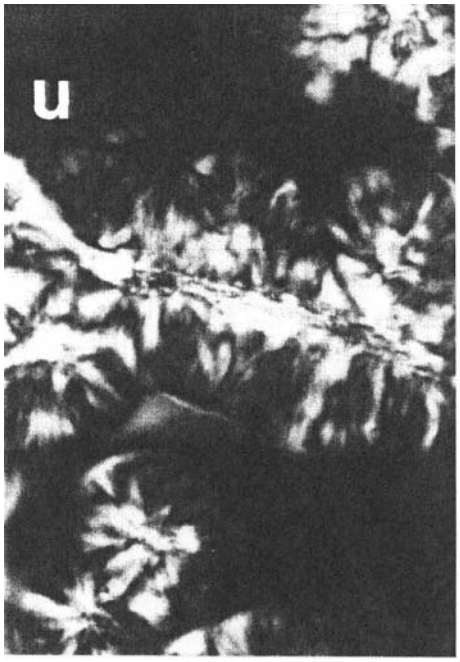


Figure 1 Fibers showing transcrystallinity in uncoupled kenaf–PP composites.

Figure 2. Fibers showing transcrystallinity in coupled kenaf–PP composites, with MAPP as the coupling agent.

zone and the neighboring spherulites or (when two fibers are close together as a result of high fiber volume fractions) adjacent transcrystalline zones. For the uncoupled systems, the interaction between the fibers and the transcrystalline zone is limited to dispersive forces, topographical effects and normal shrinkage stresses. In the case of the coupled system there are the additional factors of covalent and acid–base interactions. The interface strength between the transcrystalline zone and neighboring spherulites or the transcrystalline zone from neighboring fibers depends on molecules bridging between the crystals. Long molecular chains are important to maximize the effectiveness of the 'physical crosslinking'. The presence of low molecular weight chains will likely reduce this interface strength.

Interface failure can occur either at the fiber surface interface or the outer crystalline zone interface. Earlier work suggests that tensile and flexural strengths of kenaf–PP composites increase with small amount of MAPP addition to the blend [2]. This suggests that the addition of MAPP increased the fiber–transcrystalline zone interface strength. Addition of more than 3% (by composite weight) of MAPP reduces strength of the composite [12] and the failure shifts to other regions. This is possibly due to the presence of larger amounts of lower molecular weight polymer, reducing the strength of the physical cross-links between crystals and also between the fiber surface and the transcrystalline zone. Secondly, the transcrystalline zone of the coupled composites has more defects that could lead to failure at low strains.

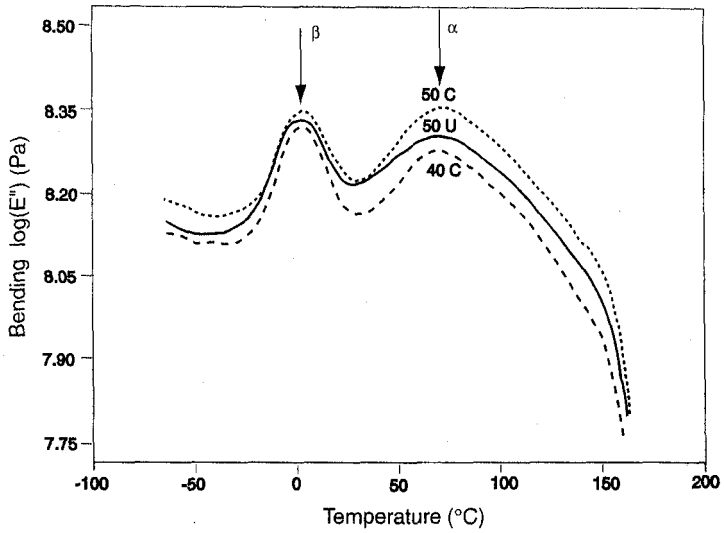


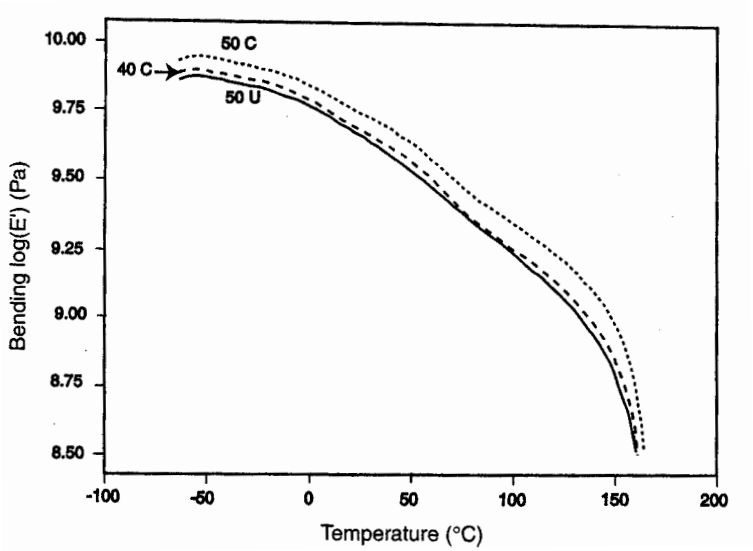
Figure 3. Variation of loss modulus with temperature of 40% and 50% by weight of kenaf in PP (C: coupled and U: uncoupled).

Figure 3 shows the loss modulus versus temperature curves of 40% and 50% coupled and 50% uncoupled kenaf–PP composites. The β-transition can be seen at around 0°C, while the a-relaxation peak can be seen between 70°C and 80°C. The a-transition is related to the relaxation of restricted PP amorphous chains in the crystalline phase. The presence of crystals is necessary for this transition to occur [13–15]. The β-transition, related to the glass-rubbery transition, is due to molecular motions associated with unrestricted amorphous PP [16].

Comparing the 50% blends, the β-relaxation (the glass–rubbery transition of the amorphous matrix) strength was higher for the uncoupled system than the coupled composites and these intensities were 89.1 MPa and 81.5 MPa, respectively. This indicates more amorphous PP chains were involved in the transition. This is possibly due to the restricted mobility provided to the MAPP molecules due to covalent bonding with the fiber surface and acid–base interactions between neighboring anhydride groups.

Figure 4 shows the storage modulus of the three composites. The uncoupled system (50%) had a lower modulus, all through the temperature range, than both the coupled composites. The softening temperatures of the coupled blends were higher than the uncoupled blend. This clearly demonstrates the effectiveness of the MAPP in improving composite efficiency. The transition, seen as the drop in modulus at around 75°C, appears to be stronger for the coupled systems indicating the presence of the restricted amorphous molecules.

Figure 5 shows the loss modulus of 20% to 60% by weight kenaf–PP composites and that of PP. Comparing the coupled composite β-relaxations with that of pure PP (Fig. 5) it is clear that there is an increase in the molecular mobility of the amorphous phase with the addition of fibers and coupling agent. Several



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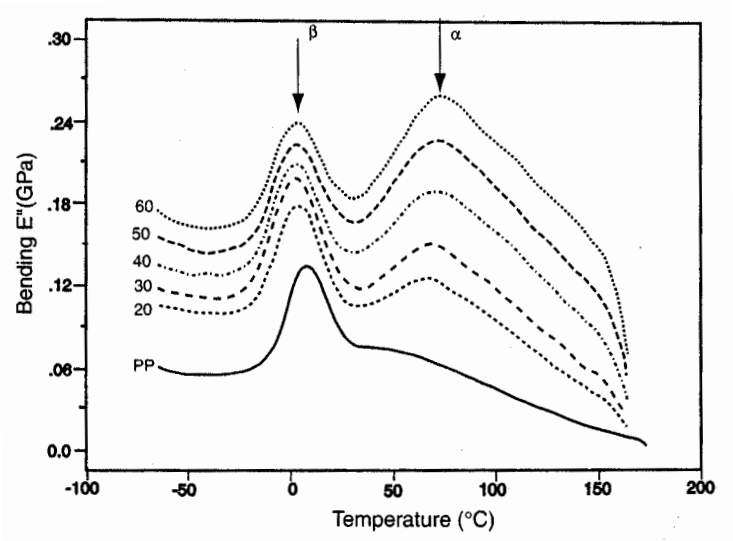

Figure 5. Variation of loss modulus versus temperature. (The numbers to the left of the curve indicate % of kenaf by weight. All kenaf composites were coupled.)

factors need to be considered to explain this phenomenon. The presence of low molecular weight MAPP could reduce the transition temperature by enhancing the ability of the polymer to undergo a glass–rubber transition [17]. Good interaction (covalent or acid–base) between the MAPP and the lignocellulosic surface restricts the mobility of the molecules and increases the β-peak temperature. Acid–base interactions between the anhydride groups of the MAPP can restrict the mobility

Table 1.
Crystallinity data, based on matrix amount, PP and kenaf composites. (All coupled samples had 3% by weight of MAPP)

Fiber weight fraction	T_c (°C)-peak	Onset T_c (°C)	T_m (°C) peak	% crystallinity (χ)
PP-100%	110.63	116.33	161.70	44.5
20-PP/MAPP	120.63	124.70	163.70	44.9
30-PP/MAPP	119.96	124.34	163.70	46.7
40-PP/MAPP	122.63	126.42	165.00	44.0
50-PP/MAPP	122.63	126.51	164.33	45.3
60-PP/MAPP	122.96	127.12	163.67	44.1
50-PP-no MAPP	122.63	126.93	164.03	46.3

Pure PP crystals: crystallization enthalpy = 209.3 J/g.

of the molecules. An important factor that has been neglected previously is that, during blending, some of the surface matrix material of the kenaf fibers themselves is sheared off from the fiber and blends in with the matrix. This sheared material could contain lignin and cellulose, and oils and other surface extractives that are inherently present in the fiber. This can be clearly seen as the dark brown tinge of the polymer matrix after blending. In other words, the matrix material is a blend of PP and several constituents that are contributed by the fiber.

Looking at Fig. 5 it is clear that factors that lower the β-peak dominate when comparing the coupled composites with that of PP. Prior work on pure and unfilled PP by Jarvela *et al.* [17] indicated that the β-peak shifts to higher temperatures with the addition of MAPP, suggesting that the MA–MA interactions dominated over the lubricant effect. Therefore, the shift of the β-peak to lower temperatures with the addition of kenaf to the matrix, is probably due to the presence of sheared surface material from the fibers. The β-peak for the uncoupled blend was only marginally lower than that for the coupled blends (Fig. 3) and this is possible since the sheared tinaterial contribution to lowering the peak dominates.

The crystallinity of PP in all the composites were about the same from DSC data (Table 1). It must be noted that due to the small sample sizes for the DSC (9 to 11 mg), it is not possible to get the precise fiber content to obtain the exact degree of crystallinity. The only clear distinction from the DSC results is that the filled Systems had higher crystallization temperatures (T,) than the unfilled systems, and the higher weight filled composites (40% and greater) had higher T_c than the lower weight filled composites. This is a consequence of a transcrystalline phenomenon which allows the PP chains to crystallize at higher temperatures, i.e. more easily.

The T_α relaxation in semi-crystalline polymers is due to the presence of amorphous chains in the crystalline phase (defects) also known as 'rigid' amorphous molecules [14, 15]. A very interesting empirical relationship was observed! The peak amplitudes or intensities of the 20, 30, 40 and 50 and 60% fiber blend (all weight percent) were proportional to their respective *fiber volume fractions* (V_f) es-

Table2.
Intensity of the α-relaxation for the coupled kenaf composites

Fiber weight fraction	Estimated fiber volume fraction-V_f (%)	Intensity (MPa)	Intensity/ V_f
60	47.79	76.52	1.60
50	37.89	60.87	1.61
40	28.92	45.22	1.56
30	20.73	33.91	1.64
20	13.24	20.87	1.58

timated from specific gravity data (Table 2). The a-peak amplitude or intensity is the E'' increase from the onset of the a-transition to the peak of the transition. The similarity in the ratios of the intensities to the V_f is remarkable. This proportionality should also hold between in the intensities and the fiber surface area. It is thus possible that the defects in the crystals that cause the T_α-transition for kenaf–polypropylene composites are predominantly near the fiber–matrix interface and exist in the transcrystalline zone.

Comparing the 50% coupled and uncoupled samples (Fig. 3) indicates that the intensity of the uncoupled samples was about two-thirds that the coupled composite. The restricted mobility of the molecules due to the presence of the solid fiber surface cannot thus be ignored in terms of defects created in the transcrystalline zone. In the case of the coupled blends, some of these defects are due to the co-crystallization of the MAPP and PP and others due to the presence of the solid fiber surface.

There is a possibility that other factors contribute to the damping. Factors include particle–particle slippage and particle–polymer interface [18, 19]. However, these factors will most likely be less in the coupled systems, where the interaction between filler and the polymer is covalent bonded, as compared to the uncoupled systems. From Fig. 3, the intensity of the a-relaxation is higher for the coupled system than the uncoupled blends. This would suggest that, although other damping mechanisms may be present, it is the defects or the rigid amorphous molecules in the transcrystalline zone that dominate the transition.

Earlier work [17] showed that in unfilled MAPP-PP blends, the T_α-peak decreased with an increase in MAPP content due to an increase in crystal defects. For kenaf composites, the a-peak shifted to higher temperatures with higher amounts of fibers present. In all blends the amount of MAPP present was 3% by weight of the composite. The concentration of MAPP present in the polymer phase increases with a decrease in matrix volume fraction and an increase in the fiber volume fraction. MA–MA interactions in the crystalline phase are more likely when the anhydride moieties are closer to each other, as in the higher fiber volume fraction composites, resulting in a shift of the a-peak to higher temperatures.

The behavior of the interphase is dominated by the characteristics of the crystals. In the case of the uncoupled system, defects are formed in crystals due to restricted

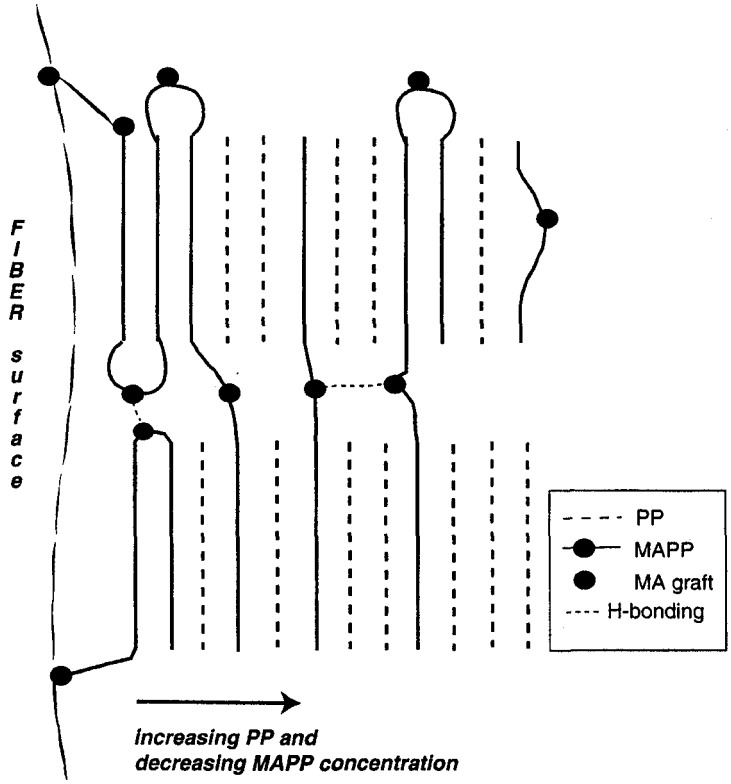

Figure 6. Schematic, in two dimensions, of the fold surface of a lamellae. Sharp folds that are representative of good packing are not shown. (MAPP molecules in dark lines.)

molecular mobility in the vicinity of a solid surface. In the case of the coupled system, two independent crystalline phases (if the MAPP and PP phase separate) or a single co-crystalline phase is possible. Work by Duvall *et al.* [20, 21] suggests that low anhydride content maleated polypropylenes co-crystallize with PP. In our case, no indication of a separate crystalline phase was observed with the addition of MAPP indicating co-crystallization. So, in addition to the restricted mobility provided by the fiber surface, the presence of MAPP in the crystalline phase resulted in higher a-intensities for the coupled composites. Figure 6 is a schematic of some of the defects possible in the presence of MAPP. For H-bonding to occur between two acid groups in the grafted polymer, the atoms need to be less than about 2.4 to 3.2 Å apart, which is more likely to happen in low matrix volume fraction (highly filled) composites where the concentration of MAPP in the matrix phase is higher.

4. CONCLUSIONS

A new 'solventless' technique to prepare samples to observe the transcrystalline zone indicated that the zone is formed for both coupled and uncoupled kenaf

fiber–PP composites. Dynamic mechanical analysis suggests that the transcrystalline zones contain a significant amount of defects. The intensities of the α-relaxation (E'' spectra) of the coupled composites were proportional to the fiber volume fractions. This may be due to the presence of MAPP in the transcrystalline zone and also to the presence of the solid surface which limits the packing efficiency of the crystals.

The molecular weight and amount of grafted MA are important characteristics of the coupling agent. Longer molecular chains and lower anhydride content could result in crystals with fewer defects. The presence of highly grafted molecules leads to poor crystal packing efficiencies. A minimum amount of MA is necessary to obtain good stress transfer and this is due to a strengthening of the fiber surface–transcrystalline zone interface. Longer molecules help in strong physical cross-links between transcrystalline zones and adjacent spherulites or adjacent transcrystalline regions, and also between the fiber surface and the transcrystalline zone.

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