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Recycling Pressure-Sensitive Products

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March 19, 2012

$$\text{Removal Efficiency (\%)} = \frac{\exp\left(\frac{T_{50} - T_R}{\alpha}\right)}{1 + \exp\left(\frac{T_{50} - T_R}{\alpha}\right)} \times 100\%$$

The efficient control of contaminants such as metals, plastics, inks and adhesives during the processing of recovered paper products determines the profitability of recycling mills. In fact, it is arguably the most important technical obstacle in expanding the use of recycled paper.¹⁻⁴ An especially challenging category of contaminants to manage is pressure-sensitive adhesive (PSA). PSAs are soft elastomer-based materials that are highly viscous and sticky to the touch. In recovered paper, they are usually found as part of pressure-sensitive (PS) label systems, consisting of facestock coated with a 0.7-1.0 mil layer of PSA.

During the initial stages of the paper recycling process, the bonds between fibers are broken using water and mechanical energy. This operation, known as repulping, also fragments adhesive films. Much of the removal of these fragments in the recycling process occurs at the pressure screens and is governed mainly by the size and shape of the residual adhesive. The PSA that is not removed by screening is introduced into the remaining fiber recovery operations and the papermaking process, where it can significantly diminish production efficiency and product quality.⁵⁻⁷

A widely acknowledged approach to reduce the negative impact of PSA on paper recycling is to design adhesives for enhanced removal early in the recycling process. Given the high efficiency of particle removal demonstrated by screening operations, the most promising PSAs are those designed to generate larger residual particles.

Our recent research efforts have focused on developing guidelines for producing these types of PS products. This article includes the rationale for our test methods to gauge screening removal efficiencies, the identification of properties controlling the fragmentation of both hot-melt and water-based PSAs, and a discussion of the role additives and laminate design play in determining the fragmentation behavior of adhesive films.

MEASUREMENT OF PSA REMOVAL EFFICIENCIES

While mill trials would be the best way to determine which PSAs are problematic, they are expensive and the results are often difficult to interpret. Fortunately, the U.S. Postal Service (USPS) provided the resources required to test the same set of adhesives on a lab, pilot and mill scale.⁵ Based on the work sponsored by the USPS, a laboratory-scale test method has been developed by a subcommittee of the Tag and Label Manufacturers Institute (TLMI).⁸ These specification and test methods have been shown to correlate with other tests and are gaining wider acceptance.⁹

For this work, we have focused on Adirondack Plastic and Paper Recycling's high-consistency laboratory repulper, and a gravity-flow flat screen from Valley Plastics and Paper Recycling. The repulper is equipped with a heating/cooling jacket and connected to a recirculating water bath to maintain temperatures during testing within $\pm 2^{\circ}\text{C}$ of targets. The test requires only about 1.5 g of PSA film and an additional 300 g of conditioned paper, which includes the label facestock (~ 5 g), envelope-grade substrate (~ 8 g), and copy paper (287 g). Laminates and the copy paper are repulped for 30 minutes in 3 L of tap water, and the resulting fiber slurry is passed through the flat screen, which is equipped with a 0.015-in. slotted screen, wider than the 0.006-0.008-in. slots found in fine screens in typical fine paper recycling operations.

For this test, the amount of PSA rejected at the screen is measured gravimetrically. Screening rejects are composed of PSA particles, as well as cellulose fiber. The fiber is dissolved in copper (II)-ethylenediamine (CED), and the adhesive particles are isolated via filtration and dried at 105°C to a constant weight. Rejected PSA mass is reported as a removal efficiency, which is the percentage of PSA mass added to the repulper that is rejected at the screen. Tested PSA films are soaked in CED aqueous solutions and dried at 105°C for extended periods to determine the mass loss of PSA additives (e.g., emulsifiers and tackifiers) during the analysis. Losses are usually found to be negligible. The details of this procedure are available elsewhere.^{10,11} Reproducibility of removal efficiency measurements was determined to be $\pm 3\text{-}4\%$.

OPTIMIZING THE REMOVAL OF PSA FILMS

Water-based acrylic PSA dominates the PS label market and, along with hot-melt PSAs, composes most of the PSA used to produce labels." By providing guidelines for making these two types of PSAs more recycling compatible, the majority of adhesives presented to recycling mills could be reformulated.

Hot-melt adhesives have phase transitions near typical recycling temperatures. If the repulping temperature is high relative to these transitions, the adhesive is soft, allowing it to break down more easily and form smaller fragments. The fragmentation of a water-based PSA is controlled by its

strength in aqueous environments. This is determined in large part by its water resistance, which is reduced by the presence of surfactants, which are needed for synthesis and formulation, and the greater polarity of the adhesive polymer. In general terms, the fragmentation of hot-melt PSA films is controlled by temperature, while the residual strength under high moisture conditions controls the fragmentation of water-based adhesive films.

The goal is to limit the extent of PSA fragmentation during repulping operations. The focus is on the films themselves, so additives and laminate designs are held constant for most of the tests reviewed here to provide for direct comparisons. As will be shown, relatively minor modifications (that do not compromise performance or costs) can be used to substantially increase the screening removal efficiencies of PSA films.

HOT-MELT FILMS

The term *hot melt* simply refers to the ability of the adhesive to melt upon heating, allowing it to be spread or coated onto a substrate. In practice, this terminology typically refers to PSAs that employ block copolymers, which combine styrene segments with those composed of monomers possessing lower glass-transition temperatures in their homopolymer form. These so-called rubbery blocks are often composed of ethylene-propylene, ethylene-butene, isoprene or butadiene. The incompatibility of the styrenic and rubbery blocks provides these polymers with separate microphases and phase transitions, which are apparent in dynamic mechanical analysis (DMA) thermoscans.

Figure 1 shows DMA data for a commercial hot-melt PSA measured over a broad temperature range ($X = 10$ rad/s, shear mode). The lower temperature transition is the glass transition for the rubbery blocks; the higher temperature transition is associated with the styrene phase glass transition and/or disruption temperature at which the interactions between styrene functional groups that provide the residual cohesive strength (sometimes described as physical crosslinks) are mostly eliminated.

Figure 1 also shows the location of the shear adhesion failure temperature (SAFT). The SAFT can be described as the temperature at which highly rapid deformation is found for the PSA, producing a failure response. In practice, it is an indication of the temperature limit on the PSA for adhesive applications. SAFT is commonly measured by laminating identical PSA labels (films plus carriers) to produce an overlap region of 1 in.² 13-14 A constant load is applied to induce a shear stress parallel to the overlapping films, and the temperature is increased until the laminate fails. This temperature is reported as the SAFT.

PSA performance requires a balance between adhesive and cohesive strength. In other words, the adhesive must be soft enough to flow into a surface at low pressures to wet it, but strong enough to withstand various loads without failing. For a hot-melt PSA, this balance is achieved within the plateau region of the adhesive (see Figure 1), which is bracketed by its phase transitions. "The cohesive strength of a hot-melt PSA declines with increasing temperature throughout the plateau region.

This loss of strength corresponds to an increase in the degree of fragmentation of PSA films during repulping operations, as well as a decrease in their removal via screening operations. In fact, removal efficiency drops from 100% to nearly 0% over the plateau region. "This behavior is fit by an empirical sigmoidal function relating screening removal efficiency to repulping temperature (T_R) of the form (see equation), for which α determines the width of the sigmoidal curve and T_{50} is its inflection point corresponding to a removal efficiency of 50%. In addition, linear correlations were

found between and the thermal width of the plateau region (ΔT) and between T_{50} and SAFT. Thus, an empirical predictive equation is formed by substituting these parameters into the equation.

The effectiveness of this approach for predicting screening removal efficiencies was shown previously with both model and commercial hot-melt PSAs developed with various types and concentrations of tackifying resins, processing oils, and styrenic block copolymers.¹⁰ An example of the data collected in this study can be seen in Figure 2, which shows the fit of laboratory repulping and screening data for a commercial hot-melt PSA. The data are fit by the model using the thermal width of the plateau region and the SAFT for the PSA.

The general applicability of this predictive equation simply demonstrates the importance of the styrene transition corresponding to a loss in its strength contribution as measured by quantities such as SAFT. Specifically, modifications that increase the SAFT relative to temperatures at which the PSA is being repulped, which typically occurs between 45 and 50°C, will reduce the extent to which it is fragmented and increase its screening removal efficiency.

WATER-BASED FILMS

Water-based adhesives are formulated and processed as aqueous dispersions. The adhesive polymer is produced via emulsion polymerization, which requires the emulsification of reacting monomers and generates a latex dispersion. This colloid or neat latex can serve as the basis for numerous PSAs produced through the addition of different types and concentrations of tackifying dispersions and additives (e.g., wetting agents, defoamers and rheology modifiers) that facilitate coating operations.

Here, the behavior of the base emulsion is separated from that of the formulated product. The difficulty is that the latex must be coated onto a release liner without the aid of a wetting agent. Through some trial and error, it was found that an acceptable film can be coated with the use of certain rheology modifiers that were found to have a negligible affect on the fragmentation behavior of the PSA.

Initially in this study, 25 label-grade and general-use adhesives were investigated. This provided a broad range of monomers, surfactants and properties. Previously published studies had claimed correlations between screening removal efficiencies and performance properties of the adhesive, but these were not evident in this study.¹⁵ Guo et al. reported that “highly hydrophobic polymers yielded larger adhesive particles that were easily removed during the screening operation.”¹⁶ A relationship was observed between the composition of the adhesive polymer and its removal.”

The commercial PSAs studied represent 25 different monomer combinations using 15 different monomers. It was seen that those PSAs containing both vinyl acetate and acrylic acid monomers provided poor removal efficiencies. In addition, it was found that the PSAs demonstrating only modest removal efficiencies contain either vinyl acetate or acrylic acid. These results indicate that the combination of particular monomers produces a critical change in the property controlling the fragmentation of the adhesive, and this change is not apparent from the mechanical, surface, or performance properties of dry films.

Given the likely tie between mechanical strength and the tendency to fragment studies were designed to examine the impact of moisture on the strength of PSA films. A convenient method for gauging the

strength of a material is through tensile testing. However, given their highly viscoelastic nature, this is a difficult task for PSA films; it is further complicated by the need to be carried out in a temperature-controlled, aqueous environment. For our approach, 11 tensile samples are produced by coating the PSA film over two separate pieces of 25-mm-wide PET films that are placed against each other to form a continuous substrate for the adhesive. All of the films cast for this study are targeted for 1 mil (25.4 μm). The ends of the PET are not coated and serve as gripping tabs. The tests are carried out in a temperature-controlled water bath at a crosshead speed of 10 mm/min.

In using this test to analyze the commercial PSA films, the same trends identified in the removal efficiency data were observed. Kinetic studies (tensile strength vs. soaking time) showed that the changes in strength induced in PSA films occurred in the first few seconds of being submerged into the water.¹¹ These changes were substantial, but the strength quickly stabilized. It was also found that soaking PSA films prior to repulping did not change their removal efficiencies. These results indicate that once water-based acrylic films are placed in water, their properties can be very different from those of the dry films.

The information obtained from studying the commercial PSAs led to the development of model acrylic water-based adhesive emulsions, which were synthesized using the same additives and approach. The model emulsions are representative of those used in PS labels. They are composed mostly (~ 81 mass%) of soft monomers n-butyl acrylate (BA) and 2-ethylhexyl acrylate (EHA); various combinations of the hard monomers (~ 16-19 mass%) methyl methacrylate (MMA), vinyl acetate (VA) and styrene (STY); and the functional monomers (~ 0-3 mass%) acrylic acid (AA) and methacrylic acid (MAA). The specific monomer composition and various properties for the model PSAs, including removal efficiencies (RE) measured at 50°C, are shown in Table 1.

As was the case for the commercial formulations, a comparison of removal efficiencies with the monomer compositions indicates that the combination of VA and AA results in films with the lowest removal efficiencies. Keeping everything else in the formulation fixed, replacing VA with MMA or STY increases removal efficiency. Also, replacing AA with MAA increases removal efficiency substantially. The experimental Log Kow for the monomers VA, MMA, STY, AA and MAA, where Kow is the octanol-water distribution coefficient, are 0.73, 1.38, 2.95, 0.35 and 0.98.¹⁷ Log Kow has been shown to correlate with measures of a chemical's aversion to water; thus, it appears that the results are generally consistent with the hypothesis that increasing hydrophobicity enhances the removal efficiency of the adhesive polymer.*

However, it should be emphasized that only the presence of the most hydrophilic of these monomers results in low removals, and both VA and AA are required to produce the extremely poor efficiencies. Avoiding these and similar monomers appears to be of key importance in making water-based PSAs more recycling compatible. Furthermore, increasing removal efficiencies does not appear to be simply a matter of using the most hydrophobic monomers. For example, removal efficiencies were found to be reduced by replacing the harder BA ($T_g = -54^\circ\text{C}$, $\text{Log } K_{ow} = 2.36$) with the significantly more hydrophobic EHA ($T_g = -80^\circ\text{C}$, $\text{Log } K_{ow} = 4.09$). It appears that under certain circumstances (e.g., monomers possessing sufficiently high hydrophobicities), the hardness of the monomer is of greater importance, and in general, the wet strength of the PSA film is what ultimately determines its fragmentation behavior and thus removal efficiency. This is demonstrated in Figure 3, which shows the wet-tensile strength of the model PSAs, along with their screening removal efficiencies.

IMPACT OF THE COATING PACKAGE

Pressure-sensitive labels are commonly manufactured with water-based PSA via transfer coating involving the coating of latex onto a release liner and drying it to produce the adhesive film. Given that the silicone release liner will have surface energies in the range of 20-35 mJ/m², casting uniform coatings requires that the surface tension of the aqueous dispersion be reduced, which is the role of the wetting agent.

Other components commonly added to the coating package include defoamers and rheology modifiers. In screening, these additives did not appear to have a significant impact on the removal efficiencies of formed PSA films at typically used levels. It was also found that the emulsifiers used in the synthesis of PSA latexes do not substantially impact fragmentation behavior at their levels. However, wetting agents do impact removal efficiencies for some PSAs.

Figure 4 shows the screening removal efficiencies for model water-based acrylic PSAs 1, 7 and 8 from Table 1. It can be seen that the wetting agent has a substantial impact on the removal efficiency of PSA 7, a small affect on that of PSA 8 and little or no impact on that for PSA 1.

These differences have been explained by identifying two major factors that govern, in large part, the extent to which PSAs fragment during repulping operations.¹⁹ The first is the underlying strength of the film, which can be quantified via measurements such as wet-tensile tests. The second, most prevalent factor is the morphology of the film during repulping operations. It appears that the more collapsed the film, the larger the residual particles. Evidence for this can be found in optical images of residual particles from repulping operations obtained for various surfactant concentrations (see Figure 5).

Returning to the observations outlined in Figure 4, a comparison of the wet tensile strengths for the three water-based acrylic PSAs shows that PSA 8 is substantially stronger than PSA 7, which is much stronger than PSA 1. The addition of a wetting agent did not have a significant impact on the wet-strength of films, and the morphologies of all three PSAs were changed in a similar fashion. These results indicate that PSAs with strong and weak intrinsic strengths are relatively unaffected by changes in film morphology. That is, the strongest films break down little, and the weakest are highly fragmented during repulping regardless of their morphology.

Only those PSAs possessing modest strength are significantly impacted by surfactants. It should be stressed that it is not just the wetting agent that can influence removal efficiencies. For example, tackifying dispersions contain 2-4% surfactant. It has been shown that for highly tackified water-based acrylic films, the surfactant used to stabilize the tackifier dispersion has a significant impact on the removal efficiencies of adhesive films.

FACESTOCK IMPACT

For hot-melt PSAs, the facestock properties are of great importance in determining screening removal efficiencies. (This has been discussed in detail in previous publications.^{20,21}) As with the effect of surfactants in water-based systems, paper facestock additives can inhibit the collapse of adhesive films during repulping operations, leading to greater fragmentation.

This effect is most prevalent in PSAs that possess modest strengths. Fragmentation behavior for those adhesives possessing the highest and lowest strengths tends to be unaffected by morphology changes induced by the facestock. Although not discussed here, the facestock influence is mostly absent for

water-based acrylic due the presence of surfactant, which tends to promote the removal of facestock fiber from PSA film surfaces.²⁰

SUMMARY

With regard to hot-melt PSA, it is the thermal locations of the phase transitions involving the styrene (end) blocks that determine the extent to which the PSA fragments during recycling operations. Formulation of hot-melt PSAs to thermally move this transition to higher temperatures will increase their screening removal efficiencies. Also, removal efficiencies for hot-melt PSA can be estimated using their SAFT and a quantity extracted from DMA temperature sweeps, which are already commonly measured in the industry. For water-based acrylics, the extent of fragmentation is determined primarily by their wet strength.

Making relatively minor modifications to the monomer composition of the adhesive polymer can produce substantial changes in screening removal efficiencies. Surfactants used in water-based acrylics are shown to influence fragmentation during repulping. The presence of amphiphilic species of any kind, including emulsifiers, wetting agents or surfactants added by recyclers to aid in fiberization and deinking, can reduce screening removal efficiencies. While surfactants are not commonly used in hot-melt formulations, they may be added during recycling and will have a similar impact.

The goal of this presentation is not to provide specific recipes for recycling compatible PS products. Rather, general guidelines are provided that will help direct the synthesis, formulation and product design to produce more recycling compatible PS products. These guidelines are already in use by the industrial partners of this project and have led to the development of a number of commercially available glues and label designs.

Through testing at the Forest Products Laboratory, the PSA films in these products have shown a strong resistance to fragmentation and high screening removal efficiencies. It appears that this can be accomplished while continuing to meet customer specifications, including cost. It is hoped that the future will see a widespread trend toward the incorporation of these design criteria in all PS products that may potentially become incorporated into recovered waste paper.

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ACKNOWLEDGEMENTS

This research was supported by the U.S. Department of Energy, project numbers DE-FC36-04GO14309 and DE-FC07-00ID13881.

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