PROPERTIES OF WATER-BASED ACRYLIC PRESSURE SENSITIVE ADHESIVE FILMS IN AQUEOUS ENVIRONMENTS

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ABSTRACT

Water-base pressure sensitive adhesives dominate the market of adhesives applied to paper. These materials are formulated as emulsions of acrylic polymers in water. Surfactants are used to stabilize the hydrophobic polymer particles. When water-based adhesives are dried, particles coalesce and surfactant segregates to interparticle domains that provide pathways for water to enter the adhesive film. Atomic force microscopy, under humidity controlled conditions, has been used to characterize formation of these structures in adhesive films. Surfactant rich domains, which strongly interact with water, lead to dramatic differences between the wet and dry mechanical properties of adhesive films. The efficiency of adhesive removal by slotted screening was observed to correlate with wet tensile strength for a set of model adhesives. In contrast, dry tensile strength is not useful for predicting performance during recycling operations.

INTRODUCTION

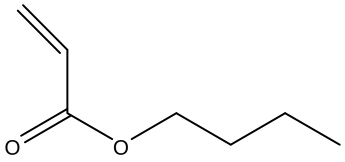
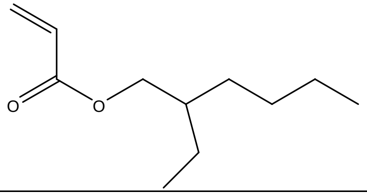
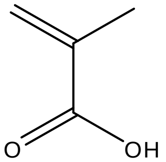
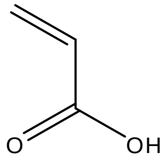
Residual pressure sensitive adhesive (PSA) particles found in recycling operations are often described as hydrophobic contaminants.[1-3] However, much of the PSA in recycled paper is part of pressure sensitive (PS) label systems, which are predominantly water-based acrylics produced via emulsion polymerization. As will be discussed, the composition and structure of these materials allow them to readily interact with moisture. When water-saturated, water-based acrylic films can contain 10% or more moisture, which is held in pores and as part of the surfactant and polymer domains. The moisture plasticizes the adhesive film reducing its cohesive strength and enhancing its flow properties. This is seen in dramatic changes in the tack, peel and shear of films when tested in an aqueous environment. In fact, the classical description of PSA contaminants as stickies and/or tackies are misnomers in that the water-submerged PSA (e.g., during repulping) often demonstrates little tack, which largely returns upon drying (e.g., during analysis).

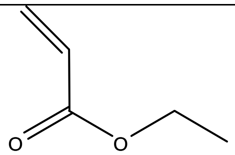
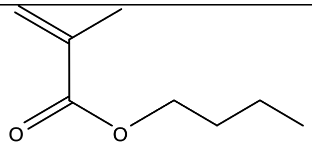
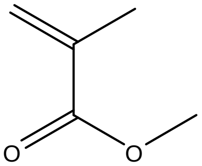
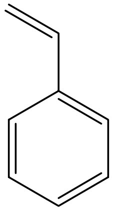
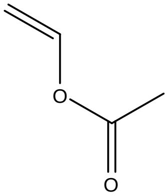
In this work, the chemical and structural characteristics of water-based acrylic pressure sensitive adhesives will be reviewed. The emphasis will be on how these characteristics provide for significant interaction with moisture and the impact this interaction has on properties that control their recycling behavior including fragmentation, deposition and removal.

DESCRIPTION OF WATER-BASED ACRYLIC PSA

Water-based acrylic PSAs are typically composed of adhesive polymers synthesized from vinyl acrylic monomers. A variety of monomers are utilized to achieve desired performance properties such as tack, peel and shear. A common method for categorizing the monomers is based on the glass transition temperature (T_g) of their homopolymers. This approach divides monomers into the categories soft, medium, hard and functional. Soft monomers produce homopolymers with T_gs below about -30 ºC, for hard monomers it is above 30 ºC, and those that produce homopolymers with T_gs between these values are considered medium monomers. Examples of each are provided in Table 1, which also includes examples of functional monomers. A typical PSA used in labels consists primarily of soft monomer. This is what provides the PSA with its viscous characteristics, i.e., its flow and wetting behavior. Hard and medium monomers are added at lower concentrations to increase the cohesive strength of the adhesive film. Function monomers are used sparingly and provide charge to the adhesive polymer and a functional group by which it can be cross-linked.

Table 1: Monomers commonly used to synthesize water-based adhesives

Soft Monomers		**Functional Monomers**	
***n*-Butyl Acrylate**	**2-Ethylhexyl Acrylate**	**Methacrylic Acid**	**Acrylic Acid**
			

Medium Monomers		**Hard Monomers**		
Ethyl Acrylate	**Butyl Methacrylate**	**Methyl Methacrylate**	**Styrene**	**Vinyl Acetate**
				

In its coating ready form, the acrylic polymer of a PSA formulation compose the colloidal particles of a latex dispersion. Normally, adhesive films are generated by coating the latex on release liner and then removing the water via drying. This destabilizes the colloid and coalesces the polymer particles. The resulting film, backed by release liner, is then pressed onto a facestock to produce label stock. This entire process is known as transfer coating. The handling of the water-based acrylic PSA as a hydrophobic colloidal distinguishes it from other PSAs such as hot-melt and solvent-based technology. Processing the adhesive as a water-based colloid provides many advantages, but the amphiphilic additives required to stabilize and coat the latex create a potential problem. These are retained in the adhesive and are likely free to migrate into adjacent phases such as facestock and substrate: they influence the coalescence of latex particles and the interaction between adhesive and adjacent layers, and they provide for the rapid uptake of moisture.

Figure 1 shows atomic force microcopy (AFM) images of a label-grade water-based acrylic PSA and its particle size distribution in the latex measured using dynamic light scattering (top right). Images were collected in tapping mode under a humidity controlled environment. The spherical geometry of the latex beads is still evident in the films and their sizes are consistent with the particle size distribution in the latex. It is believed that the brighter regions are the surfactant domains containing the amphiphilic materials that stabilized the latex. Doubling the emulsifier subsequent to polymerization did significantly brighten these regions for AFM images of cast films and rinsing the surfactant away resulted in a greater degree of coalescence. Characterizing the migration and fate of the surfactants and their impact on the properties of the adhesive films is a continuing area of focus for our group. The lower images show the same film under low (3%) and high (90%) relative humidity levels. It is clear from the reversal in the phase contrast images that the surfactant domains readily sorb moisture under at higher relative humidities.

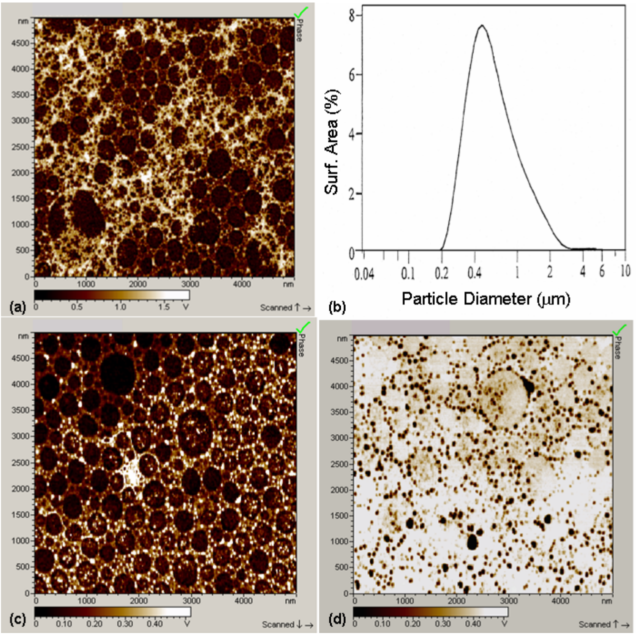


Figure 1. a.) Atomic force microcopy (AFM) image of a label-grade, water-based acrylic pressure sensitive adhesive film, b.) The particle size distribution for the adhesive in the latex, and AFM images for the film at c.) 3% and d.) 90% relative humidity.

IMPACT OF MOISTURE ON BEHAVIORS AND PROPERTIES

The description above is meant to convey the complexity of the water-based acrylic films and emphasize their tendency and ability to interact with moisture. Even if the adhesive polymer was quite incapable of interacting with moisture, the residual pore structure undoubtedly associated with the coalescence process and the presence of surfactant materials would likely provide for the rapid movement of moisture into films. With the presence of repeating units from acrylic acid and vinyl acetate, it is likely that particles of the adhesive polymer itself also take in water, which will modify their stiffness and strength.

Wet Cohesive Strength and Tack

A PSA must flow under low pressures to wet a substrate while maintaining a certain degree of strength to provide a bond between two adherends. These properties tend to be at odds with each other, i.e., increasing the ability of an adhesive to flow and wet is accompanied by a reduction in strength. Performance testing is commonly used to gauge the properties of PSAs. These usually include measures of tack, peel and shear. Tack is a measure of the ability of an adhesive to rapidly wet a surface and form an adhesive bond. In practice, tack measurements gauge the force or energy necessary to separate two surfaces that are brought together at low pressure (e.g., < 0.1 Pa) for a short period of time, usually just a few seconds, thus tack tests are often referred to as a gauge of the adhesive's aggressiveness. Shear testing involves the application of a constant shear stress to a laminate. This is commonly done by attaching a weight to the backing material of a label that is bonded to a stationary surface such as a stainless steel plate. Results are reported as the time required for the eventual failure of the laminate, which typically results from a splitting of the adhesive layer or cohesive failure. For this reason, shear results are considered a gauge of the (cohesive) strength of a PSA.

Figure 2 shows both wet (1 minute of soaking in water at 22 °C) and dry (22 °C and 50% humidity) probe tack and tensile strength measurements for 24 commercial water-based acrylic PSAs. The probe tack tests involved the use of a 1 mm spherical probe. 25 μm PSA films backed by 50 μm PET film were loaded to 0.5N of force and held for 15 s before removing. The maximum force measured during it removal is reported here. Tensile tests were used in lieu of shear testing because the water submerged shear tests produced primarily adhesive failure. Tensile specimens were prepared by transferring a 25 μm adhesive film over the joint between two PET films (25 mm wide by 75 mm long strips). The uncoated portions of the PET were placed in the tensile tester grips, and force-displacement curve was measured at 2.5 cm/min.

The results clearly demonstrate that in a water-submerged environment, water-based acrylic PSA can have substantially different properties. As will be discussed in the next section, the strength of the water-saturated films governs the fragmentation behavior of PSA films during repulping operations, and thus their screening removal efficiencies. The loss in tack is important because it is this property, which likely controls the interaction between PSA and fiber and recycling equipment. The results suggest that rather than being highly sticky materials that will likely bind to most surfaces it comes into contact with, the residual PSA particles in the recycling process are relatively benign members of the fiber slurry. However, what is not shown in the figure is the PSA's tack recovery upon drying. Much of the PSA's original tack is recovered when the PSA is dried, which accounts for its deposition and picking behavior in the drier section and beyond.

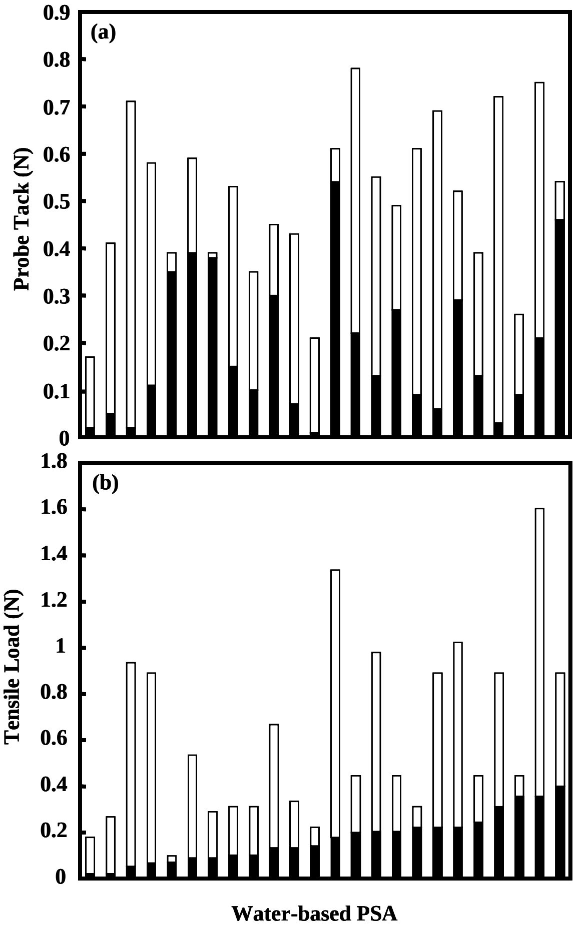


Figure 2. Measures of dry (longer bars) and wet (shorter bars) a.) Tack and b.) tensile force required to fail the films for 24 commercial water-based acrylic PSAs.

Fragmentation and Removal Efficiencies

As was discussed in detail in a previous publication,[4] the wet-strength of a water-based acrylic PSA governs its screening removal efficiency subsequent to repulping. It was shown that water-based acrylic PSA films swell rapidly and saturate in a matter of a few seconds, and hence the swelling kinetics play little role in determining the behavior of PSAs during repulping operations.

The fragmentation of the films appears dependent on the monomer composition of the base elastomer. It was found that the use of both vinyl acetate and acrylic acid monomers produced PSA that readily broke down during repulping operations and low screening removal efficiencies.

Model systems were developed for which the monomers of a commercial PSA, which was determined to have a low removal efficiency, was modified systematically by replacing its monomers with more hydrophobic versions. The "hydrophobicity" of a monomer was gauged by its octanol-water distribution coefficient. Replacing hard and functional monomers with monomers possessing higher octanol-water distribution coefficients was shown to increase measured removal efficiencies. For example, in one formulation, methacrylic acid replaced acrylic acid raising the removal efficiency by more than 50%, and in another, methyl methacrylate replaced vinyl acetate and increased it by more than 70%. It was also found that for the more hydrophobic soft monomers, hydrophobicity was not the dominant property; rather it was the strength of the homopolymer produced by that monomer. Thus, it appears the strength of water saturated PSA films determines their fragmentation behavior during repulping operations and the extent to which they can be controlled with mill screening equipment.

Given that wet-strength is the property controlling fragmentation, it would be expected that a correlation would be found between measures of wet-strength and removal efficiency. This can be seen in Fig. 3, which plots the dry (a.) and wet (b.) tensile strengths of a model series of PSAs. Superimposed on the bar charts are the screening removal efficiencies measured in the laboratory.

Little or no correlation exists between the strengths of dry and wet films or between dry film strength and screening removal efficiencies. However, a strong connection can be seen between the strength of the films when saturated with water and their removal efficiencies.

Influence of Facestock

It was demonstrated in a previous study that the paper facestock strongly influences the fragmentation behavior of hot-melt PSA films.[5-7] It was found that reducing the surface energy of the paper and/or increasing its wet-strength without preventing its eventual fiberization increases the fragmentation of the attached PSA film. For example the screening removal efficiency of a commercial label-grade, hot-melt PSA was shown to be nearly 50% lower when attached to a one-side coated commercial facestock containing papermaking chemicals that decrease its surface energy and increase its wet strength versus untreated paper containing no additives. It was hypothesized that increased adhesion between the PSA film and facestock in an aqueous environment and inhibited fiberization of the commercial paper acted to inhibit the formation of adhesive particles. Thus the films possessed a more open geometry during repulping operations, which allowed for greater stress to be induced and more fragmentation.

It is expected that the water-based acrylics will behave differently from the hot-melt formulations due to their greater tendency to interact with moisture and due to the presence of amphiphilic components at the PSA-facestock interface. As shown in Fig. 1, chemicals that are used to stabilize the latex are retained by the PSA film. The distribution of these chemicals is a continuing area of investigation for our team. It is also likely that differences in chemical structure will not only impact the distribution of a surfactant in a PSA film, it will also influence the sensitivity of fragmentation to facestock properties. This assertion is based on the observation that pilot testing of various water-based acrylic PSA with a variety of laminate designs provided mixed results with regard to the role of the facestock in determining film fragmentation. This suggests that understanding the role of surfactants and facestock must include an understanding of the transport and fate of the surfactant from label production to its behavior during recycling operations. It also suggests that certification of an adhesive as benign can be a tenuous assignment. The nature of the laminate components as well as the production operations involved in its generation can impact recycling behavior. Thus, testing of the entire laminate design is advised when assessing its potential impact on recycling operations.

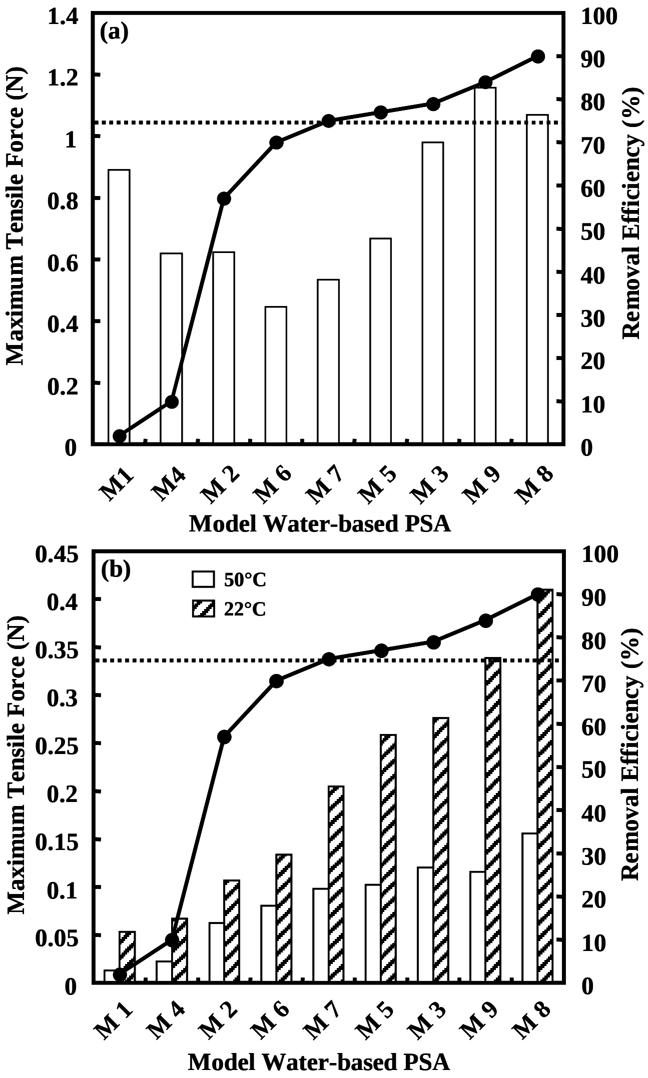


Figure 3. (a) Maximum dry tensile force values for the model water-based PSA films (21 °C and 50% RH). Superimposed are their removal efficiencies measured at 50 °C (solid dots). (b) Maximum tensile force values for the model water-based PSAs after soaking in water for 1 minute at 22 °C (solid bars) and 50 °C (striped bars). Reprinted with permission from Reference 4. Copyright 2007 American Chemical Society.

SUMMARY AND CONCLUSIONS

Although adhesive and coating contaminants found in recycling operations are commonly thought of as a single category of materials referred to as stickies, their properties can be quite diverse. The PSA materials most commonly found in recycling operations are likely either water-based acrylics or styrene block copolymer based hot-melts. While the hot-melts may well fit the above description of a hydrophobic recycling contaminant, the much more prevalent water-based acrylics are not. As described above, these adhesives are generated by coating and drying the latex to coalesce adhesive particles. These films retain the additives used to stabilize the latex dispersion. The distribution of these chemicals in the films and their tendency to migrate are not well understood. It is clear however that their presence allow for the rapid movement in and out of adhesive films. When submerged in an aqueous environment, the films rapidly swell, which substantially modifies their properties, reducing tack, adhesion and strength. The residual properties are determined by monomer composition and control fragmentation and deposition behavior in recycling operations.

ACKNOWLEDGEMENT

This research was supported in part by the U.S. Department of Energy Project Number DE-FC36-04GO14309.

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