

Properties of Pressure Sensitive Adhesives Found in Paper Recycling Operations

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Abstract

Hot-melt and water-based adhesives are very different materials with similar physical properties. Their ability to wet as adhesives is due to physical bonds and mechanical interlocks which form adhesive flows into topographical features on the substrate surface. Hot-melt adhesives are based on soft, rubbery polymers while water-based adhesives are usually acrylic latex emulsions. Both of these materials are soft and weak resulting in adhesive fragmentation during repulping. We have previously successfully modeled the behavior of hot-melts. The formulation and structure of water-based adhesives make them more susceptible to moisture when in storage, in use and in the recycling process, and thus, understanding their behavior is more difficult. Several experimental techniques have been developed to test how moisture is absorbed by adhesive and what effect water has on the performance of an adhesive material.

Introduction

Pressure sensitive adhesives (PSA) are soft polymeric-based materials that are highly viscous and sticky to the touch. They deform at low pressures to wet a variety of substrates and retain sufficient cohesive strength to provide a linkage between wetted surfaces. The wetting requirements limit the Young's modulus of PSA to below about 10^5 Pa, a restriction known as the Dahlquist criterion.¹ The balance of adhesive and cohesive strength is achieved through the proper choice of base elastomers and manipulation of their phase behavior and physical interactions using additives such as tackifying resins and plasticizers. A wide variety of PSA systems are utilized commercially, but for label applications, water-based and hot-melt formulations dominate.² Although these adhesive systems can be used to manufacture labels with similar performance at a comparable cost, they vary significantly in their chemical composition and processing, differences that influence their interactions with moisture and behavior during recycling operations. In this presentation, the composition and properties of water-based and hot-melt PSA are reviewed with an emphasis on differences that govern the fragmentation during repulping and the effect of moisture on performance properties.

Discussion

Label Grade Adhesives

The most prevalent PSA in recycled paper is water-based, which composes roughly 80% of the label-grade market. The terminology water-based derives from this PSA being formulated and processed as an aqueous dispersion. The adhesive polymer is produced via emulsion polymerization which requires the emulsification of reacting oil and generates a latex dispersion (Figure 1a). This colloid serves as the basis for numerous PSA formulations produced through the addition of tackifying dispersions, crosslinking agents and additives that facilitate coating operations including wetting agents, defoamers and rheology modifiers. The most common water-based PSA are acrylics, which combine so-called soft, hard and functional monomers to achieve a variety of performance properties. The homopolymer of the soft monomers have a glass transition below about -40°C . The most common are 2-ethylhexyl acrylate, n-butyl acrylate and iso-octyl acrylate. Hard monomers such as methyl methacrylate, vinyl acetate and styrene produce homopolymers with glass transitions above about 30°C . Functional monomers such as acrylic acid, methacrylic acid, maleic acid and acrylamide stabilize the latex and provide the PSA polymer chain with reactive groups where additional chemical reactions can occur.

Hot-melt PSA accounts for about 20% of the label-grade market. These formulations are less complex than water-based RUC, consisting of only a few components. The "hot-melt" simply indicates that the material can be melt processed. Common hot-melt formulations contain roughly equal parts of a base polymer or polymer blend, tackifying resin and plasticizer (Figure 1b) with a low concentration of stabilizer, e.g., 1-2% added to inhibit degradation. The base polymers are block copolymers containing styrene and another monomer such as ethylene-propylene, ethylene-butene, isoprene or butadiene. The blocks are incompatible and form separate phases with different glass transition temperatures.³ The most common tackifying resins used in hot-melt RUC are derivatized rosin acids and low molecular weight hydrocarbon polymers synthesized from petroleum feedstream components. Common plasticizers utilized in hot-melt formulations include low molecular weight liquid polyisobutene and mineral oils composed of complex molecular mixtures of aromatic, naphthenic and paraffinic species. These are added to reduce viscosity, lower cost, and often can modify the T_g of the rubbery phase extending the low temperature tack of an adhesive.

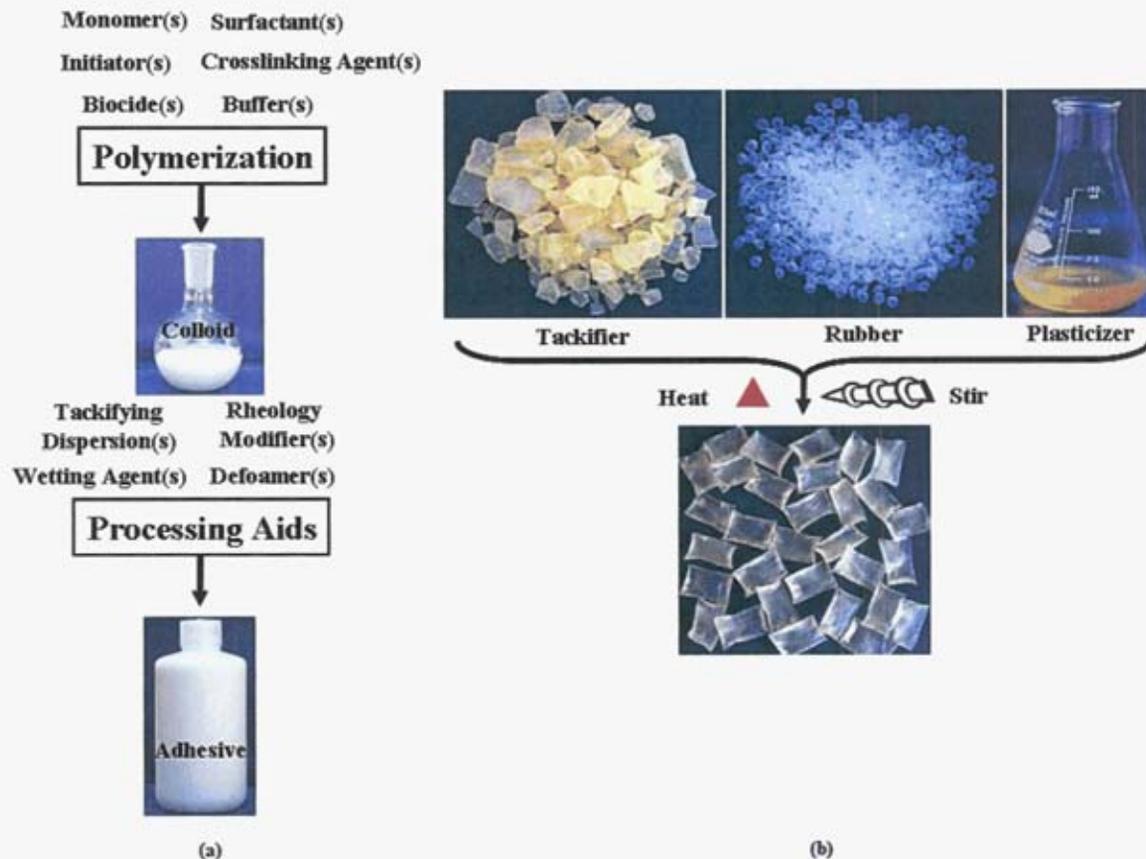


Figure 1: Water-based and hot-melt formulations

The label production is schematically described in Figure 2. Hot-melt PSA becomes molten upon heating allowing for processing including their application to carriers to produce PSA products. The energy consumption in their processing occurs during the milling and mixing operations. PSA labels are most commonly manufactured by first coating PSA onto release liner and then transfer coating and pressing the film onto facestock as described schematically in the figure.

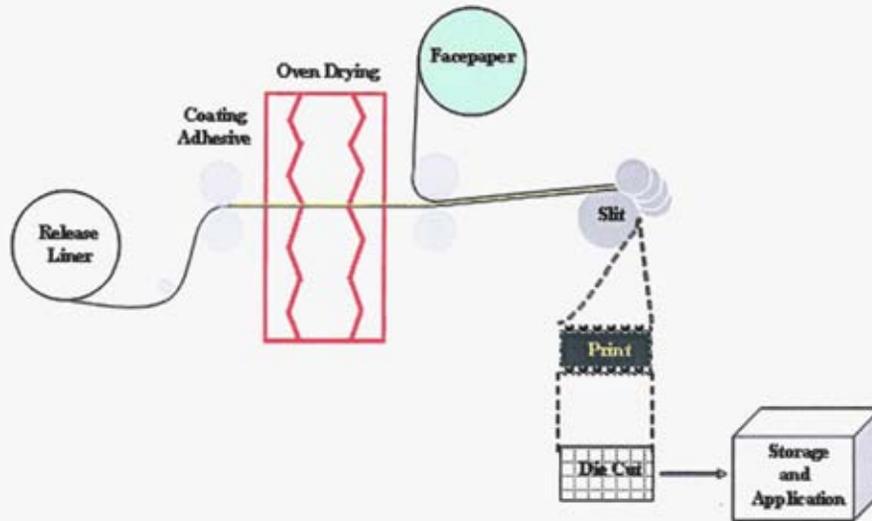


Figure 2: Manufacturing of pressure sensitive adhesive labels

Unlike hot-melt films, which are applied as a liquid then evaporate to form a continuous film, the water-based latex formulations undergo a film forming mechanism. In this process, water removal draws the latex particles into close proximity and then deforms them into a closely packed layer shown using cryogenic scanning electron microscopy in Figure 3.⁴ At temperatures above the glass transition of the polymer, the adhesive particles fuse together to form a relatively continuous film. The cost of processing these systems is associated with the energy consumed in the drying of films, which involves evaporation of significant amounts of water.

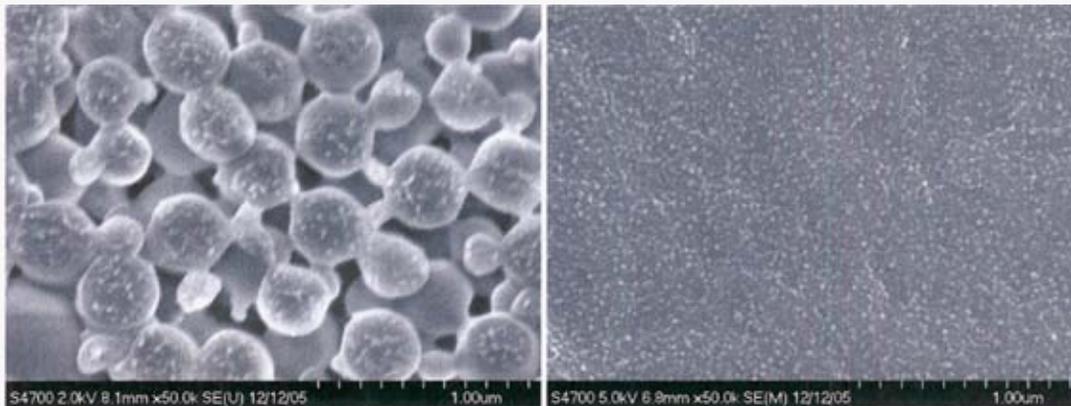


Figure 3: Water-based adhesives dry from a collection of polymer particles to a continuous solid film

Adhesive Performance Testing

For purposes of product research and development, adhesive manufacturers commonly characterized adhesives using performance testing. Performance properties include results of standard tests typically carried out on the PSA in a laminate form. The three most common are tack, peel and shear. Here, some general features of these tests are discussed. Performance measurements are meant to provide a quantitative measure of the adhesive performance. As described above, an adhesive is formulated to quickly wet a surface at low pressures and to provide a strong bond between substrates. The strength of an adhesive bond has been described as being composed of several contributions. One contribution is the ability of the adhesive to physically deform and wet out the substrate, which has both kinetic and thermodynamic aspects. Another is from the surface interactions that develop, which are

characterized by the thermodynamic work of adhesion. A final contribution is the ability of the adhesive to dissipate energy upon deformation or debonding. In practice, the force necessary to separate bonded materials is of interest, also the strength of the adhesive material itself. Performance tests are meant to provide relative measures of the aspects of an adhesive bond including the kinetics of bond formation, adhesive bond strength and the cohesive strength of an adhesive.

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 sheets that are brought together at low pressure for a short period of time. Peel tests gauge the force or energy necessary to pull an adhesive from a given surface. Peel tests are considered "cold" adhesion and are similar in many ways to tack tests, but while tack tests involve short contact times and low pressures, peel tests allow for enough contact and pressure to provide significant bonding between substrates. In other words, tack can be thought of as a measure of the adhesive's efficiency or "aggressiveness", while peel would be considered more of a measure of its strength. Even that adhesives are designed to be aggressive, tack and peel results often correlate. However, deviations from this relationship are not easily explained given the complexity of the future mechanisms involved in both measurements. 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. For this reason, shear results are considered a gauge of the cohesive strength of an adhesive. In qualitative terms, shear and tack are not to be inversely related, and it is well known that raising the shear strength of an adhesive will decrease its tack. Like tack and peel measurements, it is difficult to directly predict or identify the properties and mechanisms involved in shear testing due to the mode of failure in the sample. Regardless of the difficulties, performance testing remains a means for adhesive manufacturers to qualify their products for specific applications. Table I below compares the tack, peel and shear performance of several label grade commercial hot-melt and water-based adhesives. While the performance properties of water-based adhesives are generally lower than hot-melts, the water-based performance typically improves significantly with longer time to become more closely comparable to hot-melt properties. Another important property is the surface energy of an adhesive which is calculated using contact angle measurements. Surface energies are approximately 33-38 mJ/m² for hot-melt adhesives and 44-48 mJ/m² for water-based.

Table I: Comparison of hot-melt and water-based adhesive performance

Adhesive	180° Peel SS (lbs/inch)	Loop Tack PET to SS (N/25mm)	Static Shear (min)*
Hot-melt PSA			
HM PSA 1	6.1	80	100
HM PSA 2	6.7	64	100
HM PSA 3	6.3	144	60
Water-based PSA			
WB PSA 1	4.6	12.9	85
WB PSA 2	3.0	7.5	133
WB PSA 3	2.6	12.7	

Adhesive Interaction with Moisture

The absorption of moisture by an adhesive leads to poor performance and aesthetics in a label product. Moisture absorption is caused by a difference in moisture content between the air of the storage facility and the adhesive film. Ambient relative humidity can vary from 10 to 90% on a daily basis in various locations around the world. These conditions coupled with air temperature variations in excess of 40°C directly affect the moisture content of the adhesive label laminates. As well as ambient temperature and humidity during storage and use, moisture absorption will also affect the properties of water-based adhesive in the slurry of paper pulp and water when adhesive labels enter the repulping process for paper recycling.

Moisture sorption of the adhesive layer can vary significantly based on its structure and composition. While most polymers have no water reactivity and are resistant to moisture absorption, water-based latex emulsions contain materials that are sensitive to water. The adhesive is an acrylic polymer with small amounts of acid functional groups in the polymer chain, the acids resulting in some reactivity with water. The adhesive particles are stabilized in aqueous medium using surfactants. Unlike homogeneous polymer materials, the surfactants in water-based adhesives interact with water, also the adhesive latex structure may lead to some porosity in the adhesive film after it has been heated to 100°Cs shown in Figure 3, before drying, numerous latex particles are apparent, after drying a solid continuous film is formed. It is difficult to detect any amount of porosity in the solid adhesive film, but it can be assumed that there is some small amount of porosity and phase separation present. The chemical composition of adhesive made up of hydrophilic polymers with surfactants as well as the open packed, porous structure of the film after drying both increase its susceptibility for degradation caused by moisture.

This reactivity with water causes problems for water-based adhesives. After absorbing water, if the adhesive becomes too soft and weak then the adhesive film may no longer be able to maintain strong bonding with the substrate. The important physical effect of the absorption of water into a polymer is described as swelling. Water molecules dissolve into the adhesive polymer resulting in swelling of the polymer chain coils. This opens the polymer networks, making the adhesive softer, weaker, more plastic and more dissipative. The open polymer structure enables the polymer chains to slide past each other more readily, enabling the polymer material to flow and deform more easily, water acts as a plasticizer within the adhesive material. Swelling and plasticizing adhesive can lead to failure within the adhesive label laminate if the facestock separates from the adhesive or failure in performance if the adhesive film cannot maintain its bond to a substrate. Further changes in the adhesive occur during cyclic variations in temperature and humidity that alter the packing and coalescence of the adhesive particles. The degraded water-based film has poorer tack, peel and shear performance properties which can result in failure of the laminate product. The solid water-based film also develops a hazy, cloudy appearance when wet. This process is described as emulsifying the solid film into distinct particles which scatter light leading to the hazy appearance.

Recycling Adhesive-Containing Products

There are several contaminants in the paper recycling process such as metal, plastic and adhesive that is mixed with the paper feedstock: Many contaminants are removed by pressure screens after the paper has been repulped. This method relies on the particle size of the contaminant to be greater than the screen slot size. Adhesive on labels that enter the recycling operation has become an expensive and time consuming problem because the material is broken down into small enough particles to pass through existing pressure screens. Then, adhesive is able to agglomerate and deposit within the recycling process or continue through the mill to contaminate the resulting paper product. The cost of adhesive contaminants is several million dollars a year for machinery maintenance and poor quality paper output.⁶ While the majority of this problem has been solved for hot-melt adhesive by prior research efforts, it remains a boundary condition for further research and product development.⁷ An understanding of the recyclability problem has yet to be developed for water-based formulations.

Techniques in the past have been used to disperse or dissolve contaminants with an aqueous chemical additive and remove them with an additional cleaning processing step. The current approach of using the existing pressure screens remains the most suitable and cost effective option for removing adhesive particles. The solution to the recyclability problem is to produce, sell, buy and use adhesives that remain as large enough particle sizes when broken down during repulping to be removed by existing pressure screens. By altering the feedstock materials, it is possible to avoid the problem. Also, it has been shown that independently choosing adhesive and paper with good recyclability properties did not result in a recyclable laminate but that the interactions between paper and adhesive materials used in the laminate greatly effect the recyclability and must be chosen wisely to create a truly recyclable product. The combination of adhesive being reinforced by the paper substrate and also the ability to collapse itself into a ball or cylinder shape limits the amount of stress and strain that can be applied to the adhesive particle during repulping.⁸

Both water-based and hot-melt adhesives are problematic for paper recycling operations, although it is likely that water-based formulations have the greatest impact. Water-based adhesives are the most common within paper products that enter the recycling feedstock. Also, as stated above, they have lower cohesive strength than hot-melts and naturally deteriorate when exposed to water. During the recycling process, the high shear stresses that fragment paper and adhesive particles will cause further breakdown of adhesive if it is weakened and softened by moisture

absorption. Though moisture uptake is a slow process in polymeric materials, the increased surface area of many small particles can expedite the absorption process. While the recyclability of hot-melt adhesives has been successfully modeled using the temperature dependent phase transitions and shear strength performance, the same models cannot be applied to water-based adhesives because they lack the well defined phase transitions and water resistance of hot-melt formulations.

Current Research

By developing an understanding of how water is absorbed by an adhesive and what effect moisture has on the adhesive performance, it may be possible to engineer adhesives that do not degrade due to temperature and humidity fluctuations while in storage and also maintain large enough particle sizes to be moved during the recycling process. To do this, several techniques have been developed to measure the mass of water being absorbed and the tack, peel and shear performance while the adhesive is exposed to various environmental conditions. An environmental chamber is setup to control temperature and humidity which enables precise environmental control of space to conduct experiments within. Tack, peel and shear testing mentioned above is performed using a miniature tensiometer within the environmental chamber. Performance testing on adhesive can now be done over a broad range of temperature and humidity conditions. Also added within the environmental chamber is a sensitive balance which is able to measure fractions of a microgram changes in mass for bulk adhesive samples. Also, for use in conjunction with the environmental chamber, a quartz crystal microbalance (QCM) is capable of measuring mass changes in the ng/cm^2 range. Preliminary QCM results in Figure 4 show the difference between water-based and hot-melt adhesives when they are submerged in water, the high level of moisture absorption by water-based adhesive is apparent.

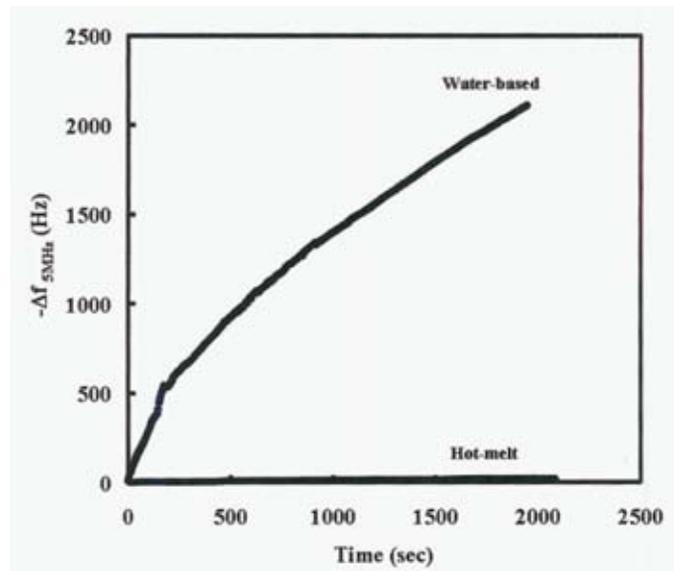


Figure 4: Moisture absorption is greater for water-based adhesives compared to hot-melts

The QCM equipment was constructed for specific application to the adhesive and moisture interactions. This system enables us to measure changes in mass and energy dissipation of adhesive films coated on the quartz crystal as they absorb moisture from the surrounding environment. Adhesive latex emulsions are spin coated onto quartz crystals. The crystals are mounted in a holder and exposed to controlled temperature and humidity conditions in the environmental chamber. Moisture sorption is measured directly as the mass of the film increase causes the resonance frequency to decrease. The Sauerbrey equation is used to describe the change in mass (Δm) on the oscillator as a function of the measured change in frequency (Δf), where the unperturbed resonant frequency (f_0), the electrode area (A), the density of quartz (ρ_Q) and the shear elastic modulus of quartz (μ_Q) are constants.⁹

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_Q\mu_Q}}\Delta m \quad (1)$$

Also, as water is absorbed by the adhesive it becomes softer and more dissipative. The energy of the crystal and film oscillations is measured using the digital multimeter. The voltage output from the multimeter can be used to quantify the change in viscoelasticity of the film being measured as it absorbs water. For QCM experiments, the viscoelasticity of a material is represented as the serial addition of an inductor, capacitor and resistor electrical circuit that is equivalent to the sample in parallel with the purely elastic quartz crystal¹⁰. In the electrical equivalent circuit, the elastic effect of two capacitors is cancelled within the QCM equipment and the inductor is assumed to be constant, leaving the resistor as a variable for the inelastic component that dissipates energy. As an adhesive film on the QCM crystal absorbs water, it becomes softer, more viscous or more dissipative, the equivalent electrical resistance (R) increases as measured by the voltage (V) output of the oscillating crystal.

$$R = 10,000 \times 10^{-5} \frac{V}{5} - 75 \quad (2)$$

The combination of frequency and voltage measurements makes it possible to study the diffusion of moisture into adhesive as well as its effect on the physical properties of the adhesive. The QCM equipment coupled with tack, peel and shear strength performance testing offers the ability to quantitatively study how fast moisture is absorbed by an adhesive, how much moisture is present within the adhesive and how water affects the ability of adhesive to stick and hold onto another material. It is possible to identify the components and properties of water-based formulations that make them susceptible to moisture absorption and relate them to changes in performance and recyclability after exposed to water.

Summary

Water-based and hot-melt adhesives in label application make up a significant portion of the pressure sensitive adhesive market. Recently, efforts have been made to study the chemical, physical and performance properties of the adhesive materials in order to lessen their impact on the recycling process and to prevent degradation from environmental conditions during storage and use. The monomer composition in the adhesive polymers and the physical structure of the final films can be used to explain some of the differences in recyclability and in performance when exposed to water. Water-based adhesive acrylic polymers with acid functional groups swell and plasticize when water is present causing them to soften and weaken. The surfactants present in the water-based adhesive formulation cause the soiled films to be reemulsified, weakening the films and creating a hazy, cloudy appearance in a previously clear film. In this presentation, we will review current research being performed to test how water is absorbed into an adhesive and what effect moisture has on the adhesive performance.

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