Development of waterborne laminating adhesive systems

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One-component waterborne adhesive systems can effectively replace solvent-borne adhesives in commercial applications.

Laminating adhesives are widely used to bond the various substrates in a multi-layer flexible packaging material. There is a wide variety of substrates available for use in these materials. Some substrates impart barrier properties, while others provide structural strength. Still others are used to lock printed surfaces beneath a clear layer of film.

Solvent-based laminating adhesives are the most widely used bonding systems. In recent years, however, waterborne laminating adhesive systems have become increasingly important to the industry, particularly as a replacement for solvent-based systems (*1*). Environmental and economic considerations, as well as the availability of better waterborne adhesive systems, are the primary reasons for this trend.

Most waterborne adhesive systems have two components. Some of these two-component systems consist of a reactive acrylic latex polymer and a coreactant. The coreactant reacts at room temperature with the acrylic latex polymer (*2*). Two-component waterborne adhesive systems have a pot life of 12–24 h. These systems generally depend on crosslinking the adhesive after lamination to obtain good cured-bond strength. Sometimes these two-component systems yield low initial bond strength.

There are also some one-component waterborne adhesive systems being used commercially. These one-component systems are based on polyvinylidene chloride (PVDC) latexes. These PVDC-based systems provide some barrier and bond strength to laminated webs. However, PVDC systems generally yield lower bond strength and require the use of noncorrosive gravure cylinders.

This article reviews the fundamentals of the adhesive lamination process, examines the basic performance requirements for an adhesive, and discusses the approach used in designing a new waterborne, latex-based, one-component laminating adhesive system.

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Dry-adhesive lamination process

The adhesive lamination process consists of two steps. During the first step, the coating adhesive is spread uniformly onto the primary web, and the diluent is removed by passing the coated primary web through an oven. During the second step, the adhesive-coated primary web is bonded to the secondary web using a heated nip roll and pressure. This process is illustrated in **Fig. 1.**

Adhesive performance requirements

An effective adhesive system must fulfill some basic performance requirements:

Wetting of primary web. When in its liquid state, the adhesive must be able to uniformly wet different types of webs at high speed and at optimum coat weight.

High bond strength. A good adhesive should combine the primary and secondary webs into a unified composite. The resultant laminated structure must have high bond strength. Such a structure will tear rather than debond.

Specific applications may require adhesives with specialized performance requirements, such as:

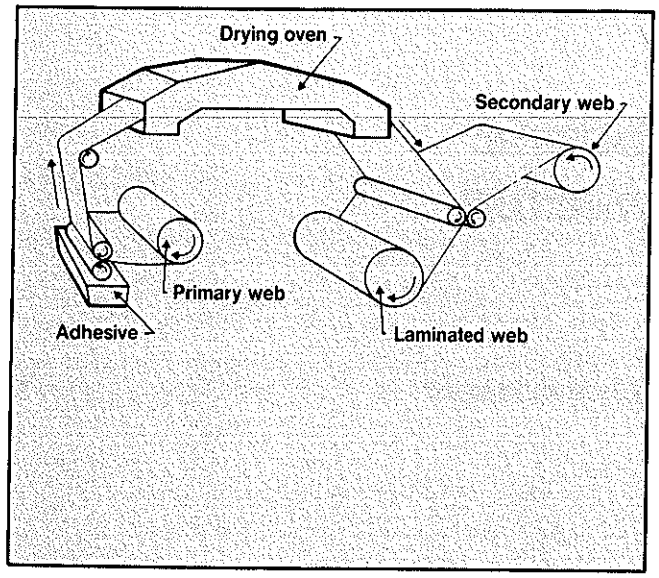
- Optical properties
- Water, heat, and chemical resistance
- Resistance to delamination and tunneling
- Resistance to discoloration.

Technical consideration in developing one-component latex-based systems

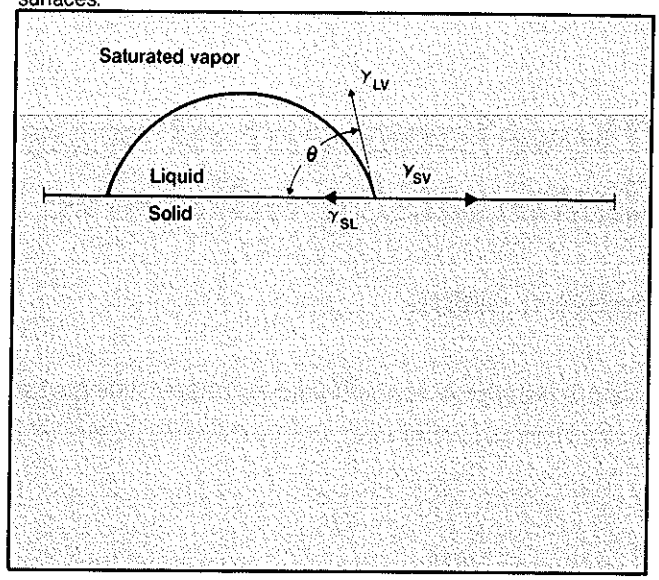
The one-component waterborne adhesive systems discussed in this article are latex based. Latexes—colloidal dispersions of polymer particles in a continuous water phase—are produced by an emulsion polymerization process. These emulsion polymers are prepared by judiciously selecting monomer types and levels. After emulsion polymerization of the selected monomers, the resultant milky white dispersion contains solid polymer particles.

The colloidal and polymer properties of a latex-based adhesive are controlled by these variables:

1. Dry-adhesive lamination process.



2. High-surface-tension liquids bead up on nonpolar, low-energy surfaces.



- Surfactants
- The monomers used to prepare the polymer backbone
- Functional modifiers
- Molecular weight/crosslinking
- Processing conditions during polymerization.

The effect of each of these variables on adhesive performance was evaluated during developmental trials for our one-component waterborne adhesive system.

Wetting of primary webs

Surface tension of substrates

There are many different types of primary webs used in flexible packaging applications. These webs include polyolefins, polyesters, polyamides, metalized films, and foil. Many of these substrates are difficult to wet because of their low surface energies, their nonpolarity, or because of the presence of slip agents. **Table I** lists the surface energies of substrates that are commonly used in flexible packaging laminations.

We have already noted that latexes are colloidal dispersions of polymer particles in a continuous water phase. Water, because of its higher surface tension (72.8 mN/m), does not spread but rather beads up on nonpolar, low-energy surfaces such as polyolefin films. This phenomenon is illustrated in **Fig. 2.**

Equilibrium spreading occurs when

$$\gamma_{SV} > \gamma_{LV}\cos\theta + \gamma_{SL} \qquad (1)$$

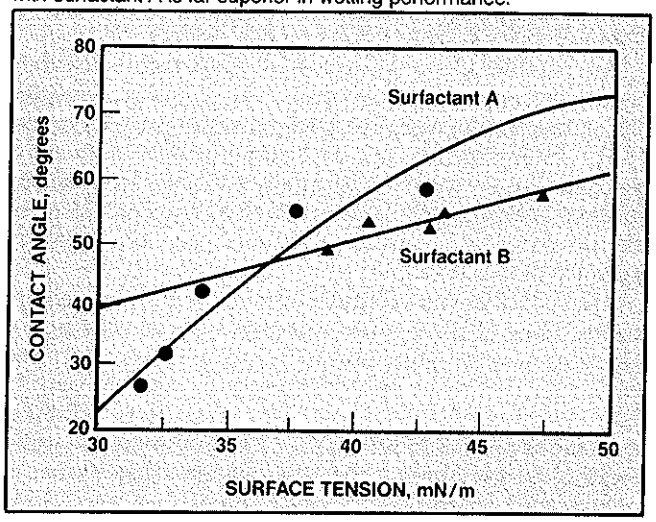
where

γ_{SV} = surface energy of the substrate

γ_{LV} = surface tension of latex

γ_{SL} = interfacial surface tension between the latex and substrate surface.

3. Contact angle of latex measured on the polypropylene film vs. the surface tension of latex for two different surfactant systems. The latex with surfactant A is far superior in wetting performance.



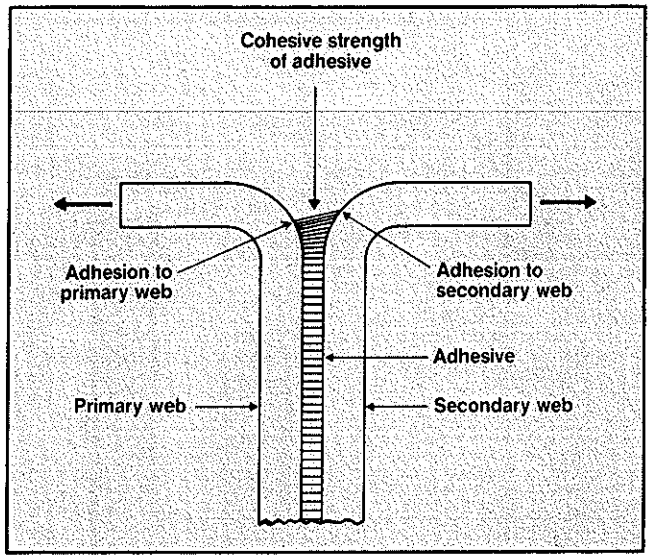
Thus wetting is facilitated if γ_{LV} is lowered or if γ_{SV} is increased and γ_{SL} is minimized. The γ_{LV} of the latex can be lowered by the addition of surfactant. It is also possible to increase γ_{SV}, the surface energy of the substrate, by corona-discharge treatment, which oxidizes the surface and imparts polar groups.

In the process of coating latex at high speed, the dynamic aspect of wetting is also critical. The wetting failure of greatest concern is the dewetting of the adhesive from the primary web between the gravure coating station and the drying oven. Two types of dewetting phenomena are possible: (a) retraction of the latex coating from the edge and (b) surface cracking (*3*).

Effect of surfactant systems on wetting

The choice of surfactant system is critical for high-speed application of a smooth, continuous, defect-free film of adhesive. We evaluated the effect of anionic, cationic, and

4. The T-peel test provides a measure of a laminating adhesive's bond strength.



I. Surface energies of commonly used substrates

Substrate	Surface energy (γ_{SV}), mN/m: Untreated	Corona treated
Poly(ethylene)	32	35-40
Poly(propylene)	29	35-40
Poly(styrene)	42	...
Poly(ethylene terephthalate)	43	...
Poly(amide)	46	...

II. Surface energies of various polymers

Homopolymer type	Surface energy, mN/m	Polarity
Poly(butadiene)	31.0	Nonpolar
Poly(butylacrylate)	35.7	
Poly(t-butyl styrene)	35.8	
Poly(vinyl chloride)	40.0	
Poly(vinylidene chloride)	40.0	
Poly(styrene)	43.1	
Poly(ethylacrylate)	46.3	
Poly(acrylonitrile)	49.0	
Poly(vinylacetate)	53.2	Polar

III. Functional polymer modifiers

- COOH	Acid
- OH	Hydroxyl
- NH_2	Amine
- $CONH_2$	Amide
- $CONHCH_2OH$	Methylolamide
- CO_2R	Ester
- CN	Nitrile
- SO_3H	Sulfonate
- CHO	Aldehyde
- C-C (O)	Epoxy

nonionic surfactant systems on the adhesive's ability to wet polypropylene film. The surfactant systems were typically evaluated by measuring surface tension with a DuNoy Tensiometer, measuring contact angle with a goniometer, and judging the wetting performance on polypropylene film.

Different surfactants lowered both the adhesive's surface tension and its contact angle on polypropylene film to different degrees. In **Fig. 3**, the contact angle of latex measured on the polypropylene film is plotted against the surface tension of latex for two different surfactant systems. It is evident that the latex with surfactant A has a significantly lower contact angle and surface tension than the latex with surfactant B. The wetting properties of the latex with surfactant A were far superior to those of the latex with surfactant B.

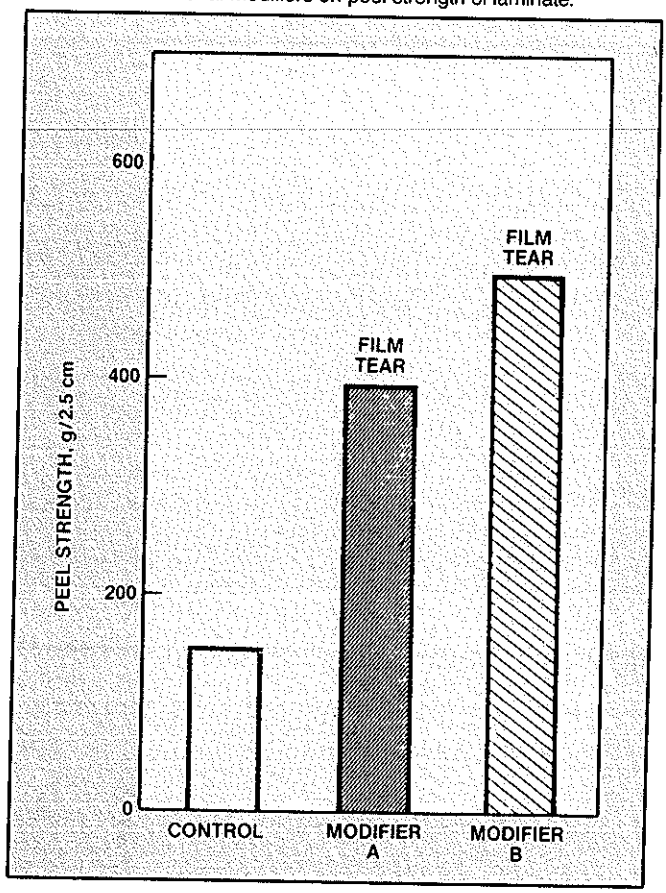
These results seem to be in agreement with those of Mahoney *et al.* (*3*). According to their results, dewetting problems can be overcome by reducing both the surface tension and the contact angle of latex as far as possible while maintaining high viscosity. Other factors that contribute to the wetting performance of latex-based systems include surface mobility, viscosity, and elasticity (*3*).

Bond strength

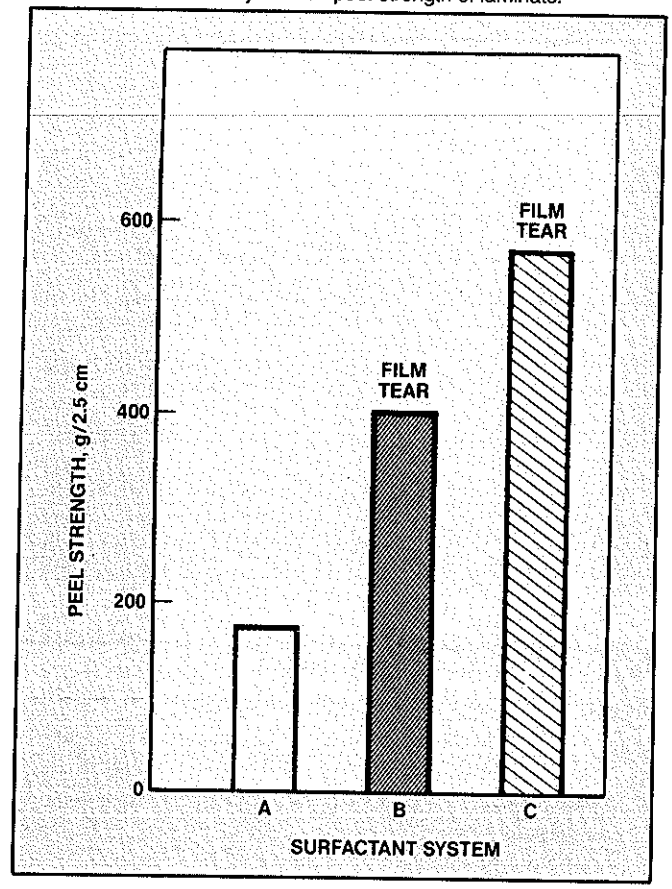
Effective laminating adhesives generally provide a high degree of bond strength at low coating weights. The bond strength of a laminate depends on both the adhesive and the cohesive strength of the adhesive system. A laminate's peel strength is typically determined by debonding the laminate on an Instron using a T-peel test. The T-peel test is illustrated in **Fig. 4**.

When a laminate is debonded, there are at least four possible modes of failure:

5. Effect of functional modifiers on peel strength of laminate.



6. Effect of surfactant system on peel strength of laminate.



- Adhesive failure (primary)—debonding of the adhesive from the primary web
- Adhesive failure (secondary)—debonding of the adhesive from the secondary web
- Cohesive failure—splitting of the adhesive itself
- Film tear—failure of the web itself.

A laminate will fail at its weakest link. If the adhesive does not fail, then failure will occur as film tear.

Energy dissipation during debonding is dependent on such parameters as:

- Interfacial adhesion
- Polymer rheology
- Rate of peel
- Temperature
- Angle of peel
- Web stiffness
- Coat weight (thickness of adhesive).

The strength of the laminate depends on the interfacial adhesion (a thermodynamic phenomenon) and the bonding (a kinetic phenomenon) of the adhesive to the primary and secondary webs. According to Dalquist (*4*), for good bonding to occur, the dried adhesive must meet the following requirements:

- Intimate contact with the web (i.e., effective wetting)
- Low viscosity in terms of segmental motion of the polymer
- Low elastic modulus and high deformability.

Polymer rheology greatly affects all of these parameters plus the cohesive strength of adhesive systems.

Various approaches have been taken to develop high bond strength in waterborne adhesive systems. For example, two-component systems were developed by modifying the techniques used to make aqueous-based pressure-sensitive adhesives (*1*). The modification involves introducing sites for crosslinking. The molecular weight of these adhesives is generally too low for use as a laminating adhesive. The molecular weight of the adhesive is increased by crosslinking reactions after the lamination step. Another popular approach is to modify the chemistry used in the manufacture of PVDC coatings. These systems are single-component curing PVDC adhesives.

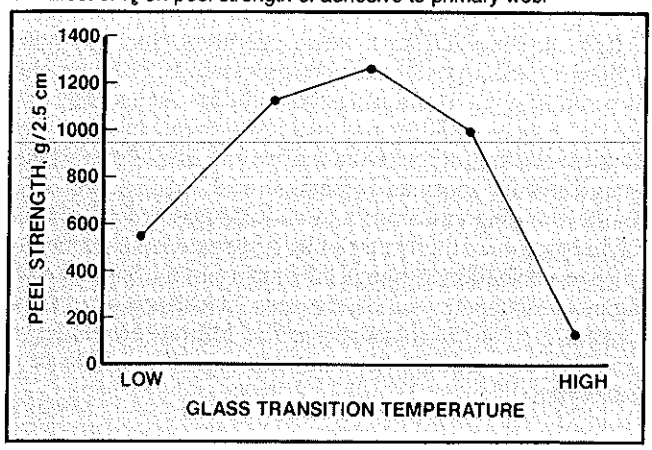
In our approach toward developing a one-component latex adhesive, we focused on optimizing the system's interfacial adhesion and its polymer rheology.

Interfacial adhesion

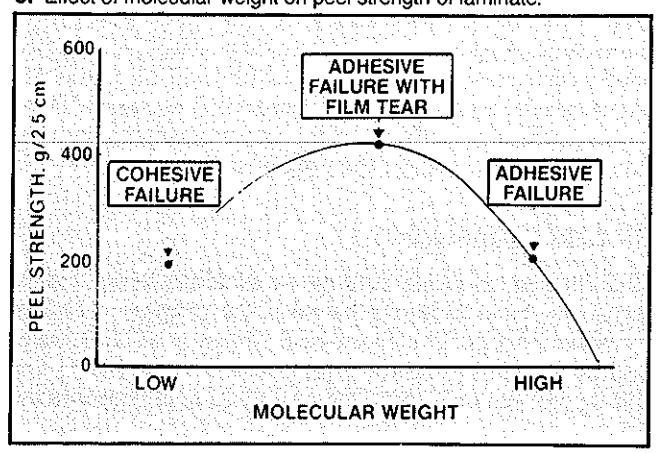
Stable bonds are formed when there is a strong interaction between the adhesive and the substrate. The different types of possible interactions include van der Waals forces, polar interactions, electrostatic interactions, and chemical bonding.

In flexible-packaging lamination, the most widely used

7. Effect of T_g on peel strength of adhesive to primary web.



8. Effect of molecular weight on peel strength of laminate.



IV. Glass transition T_g temperature of various polymers

Homopolymer type	T_g°C	
Poly(methyl methacrylate)	105	Very hard
Poly(acrylonitrile)	103	
Poly(styrene)	100	
Poly(vinyl chloride)	81	
Poly(viny acetate)	32	
Poly(vinylidene chloride)	-18	
Poly(ethylacrylate)	-22	
Poly(butylacrylate)	-54	
Poly(butadiene)	-85	Very soft

substrates are quite inert, nonpolar, and have a low surface energy. With inert surfaces such as these, chemical bonding is seldom attainable. Instead, it is useful to define the optimum matching of adhesives and substrates in terms of some measure of compatibility.

A useful approach for evaluating the compatibility of adhesives and substrates is to measure the free energy of these surfaces. Theoreticians have formulated adhesion models based on thermodynamic considerations. The surface energies of adhesives and substrates express the thermodynamic or reversible work of adhesion, W_A. That is, the change of free energy when materials are brought into contact represents the amount of work expended under reversible or equilibrium conditions to disrupt the interface. This expression is given by the following equation.

$$W_A = \gamma_{SV}\,\gamma_{LV} - \gamma_{SL} \qquad (2)$$

In practical terms, to increase van der Waals interaction of the adhesive to low-energy substrates such as polyolefins, the designed latex should also have comparable surface energy properties. The surface energies of latexes are dependent to a great extent on such variables as:

- The monomer composition of the polymer backbone
- The functional monomers and modifiers
- The surfactant system.

Monomer composition of polymer backbone

The first step in designing a one-component laminating adhesive system is the selection of monomers to synthesize the polymer backbone. **Table II** lists the surface energies of homopolymers of the various monomers commonly used for latex polymerization. The polar or nonpolar nature of a monomer is also important in the design of latex adhesive systems.

The selection of monomer composition was based on the surface-energetic requirement of adhesives to laminate a wide range of substrates. However, monomer composition also affects the glass-transition temperature (T_g) of latex polymers. Thus monomer selection is discussed later in this article, when we examine the effect of T_g.

Functional monomers and modifiers

A functional modifier is generally defined as a chemical species that can be either copolymerized or incorporated into the polymer backbone at low levels (generally less than 10%) to significantly alter the performance characteristics of a latex. Functional modifiers in the latex can significantly affect interfacial adhesion to both the primary and secondary webs. Different chemical species can be incorporated as modifiers in latex. These functional polymer modifiers are listed in **Table III**.

We prepared adhesives with various types and levels of modifiers and investigated their effects on the bond strength of laminates. The coat weight of adhesive was maintained around 3 g/m² (1.50-2.0 lb/ream).

Figure 5 illustrates the effect of different functional modifiers on the peel strength of film-to-film laminated structures. These results clearly indicate that the functional modifiers significantly increase the peel strength of laminated structures. Thus, the choice of functional modifiers is critical for obtaining a high bond strength in a waterborne adhesive system.

Surfactant system

Surfactants are chemical species that migrate to and orient at interfaces. Surfactants can exude to the interface between a dried adhesive and a substrate, thus affecting the interfacial adhesion to the primary and secondary webs. Frequently, the presence of a surfactant at the interface constitutes a weak boundary layer (*5, 6*) and has a detrimental effect on the adhesive strength.

We prepared adhesives with various types of surfactants and investigated their effects on the bond strength of laminates. **Figure 6** illustrates the effect of selected surfactants on the peel strength of film-to-film laminated structures at a coat weight of 4 g/m² (2.5 lb/ream). These results clearly indicate that bond strength can be maximized by selecting the proper surfactant.

Polymer rheology

The rheological property of the dried adhesive is a critical aspect of bond strength between the primary web and secondary webs. The rheological property of latex-based adhesives can be significantly affected by (a) the T_g and (b) the molecular weight and crosslinking of copolymers.

Glass transition temperature

The monomers listed in **Table IV** differ significantly in their hardness when they are homopolymerized. The relative hardness of a homopolymer is generally characterized by its T_g. The temperature at which polymer changes from a glassy state to a rubbery state is considered its T_g.

As mentioned previously, these homopolymers also differ in their critical surface energy. Therefore, the monomer composition for the latex adhesive system was selected on the basis of the adhesive's surface energetic and its T_g requirements.

We prepared latex adhesives with different copolymers that varied in their T_g. These latexes were evaluated for their adhesion to polypropylene film. **Figure 7** illustrates the effect of T_g on the peel strength of adhesives to a polypropylene web. These results clearly indicate that the optimum T_g is critical to the design of adhesives with high peel strength to a polypropylene primary web.

Molecular weight/crosslinking

The polymer rheology of the latex polymer is significantly affected by controlling the molecular weight and crosslinking of the latex. Reducing the molecular weight and crosslinking lowers the modulus of a polymer when the polymer is at a temperature above its T_g. A lower polymer modulus facilitates the flow of polymer onto the primary web as well as onto the secondary web during the laminating step. However, reducing the molecular weight/crosslinking also lowers the strength of the polymer. Increasing the molecular weight and crosslinking has just the opposite effect, since it hinders polymer flow onto primary and secondary web.

Latexes were prepared by systematically varying molecular weight and crosslinking. All latexes were formulated appropriately. The effect of molecular weight/crosslinking on peel strength of film-to-film laminated structures was studied. **Figure 8** shows the effect of molecular weight on the bond strength of a laminated structure. It is evident that if molecular weight and crosslinking are reduced too much, the peel strength is low and the failure mode is cohesive in nature. However, if molecular weight and crosslinking are increased too much, the peel strength is low and the adhesive fails. So, to obtain high bond strength, the molecular weight and crosslinking of the adhesive must be optimized.

Formulation technology

After choosing the base latex polymers that meet the adhesive's basic performance requirements, the next step is to develop an appropriate formulation technology that meets various end-use and customer requirements. The flexible-packaging industry is dynamic, and the substrate requirements continually change and expand. To meet these changing customer and end-use needs, formulation technology must be developed by investigating parameters such as surfactant systems, leveling systems, foam control agents, thickeners, and plasticizers. The effects of all these parameters on the performance of laminating adhesive systems are studied to meet the specific needs of a customer.

Conclusion

Regulatory, environmental, and economic considerations have significantly accelerated the conversion from solvent to waterborne laminating adhesive systems. The knowledge and application of the fundamental principles of wetting, interfacial adhesion, and polymer rheology have led to the development of one-component waterborne adhesive systems. These adhesive systems have a pot life of several months, good initial bond strength, and high final bond strength. One-component waterborne adhesive systems can effectively replace solvent-borne adhesive in a commercial production line.

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