Current and future automotive use of acrylic pressure-sensitive adhesives

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Current and emerging developments in acrylic pressure-sensitive adhesives indicate improved performance and increasing use in a number of exterior and interior applications for the automotive market.

Acrylic pressure-sensitive adhesives (PSAs) have been and continue to be important in the automotive market. This is based on their excellent thermal and ultraviolet (UV) stability, as well as on their PSA performance balance. Both emulsion and solution systems are being used in a wide variety of applications, including exterior mounting tapes, exterior graphic films, interior trim bonding, instrument displays, and foam gaskets.

Each of these applications and other emerging applications have their own unique performance balance and system requirements. However, all are relatively demanding in terms of several characteristics of PSA performance. A high degree of performance stability is generally required, and often both high peel and high shear performance are required from the same adhesive.

Some people might contend that acrylic PSA technology has been around for some time and therefore usage must be reaching a plateau. Some ideas presented here will argue for nearly the opposite train of thought. Significant advances are still possible by combining a polymer materials science approach (rather than only "chemistry") with a total systems approach (rather than working with only the adhesive), and by incorporating new chemistries and materials into "acrylic" adhesives.

The need of the automotive industry for PSAs appears to be increasing. Exterior graphics are growing in popularity. Adhesive attachments rather than mechanical fasteners are desirable from many perspectives. These expanding needs can be met with further advances in acrylic PSA technology.

Automotive applications of acrylic PSAs

We estimate the current total use of acrylic PSAs in the automotive market to be about 14 million dry pounds. **Table I** and **Fig. 1** summarize the primary current market segments by application and by typical adhesive form—waterbased (emulsion) or solvent. The primary use of acrylic PSAs is still for exterior applications because of their excellent weather resistance. Interior usage may continue to grow as the automotive industry strives for increased line speeds and lower volatile organic compounds (VOCs) in assembly operations. The use of PSAs in film form offers many advantages over mechanical attachment or sprayed-on contact adhesives. Acrylic PSAs are well positioned to share in this growth, based on their excellent performance across a broad range of environmental conditions.

Table II is a partial list of emerging automotive applications for acrylic PSAs. As acrylic PSA technology improves, the list should expand.

Automotive application requirements

Tables III-V present the types of adhesive requirements in three of the currently more important automotive applications: exterior mounting tape, exterior graphic films, and interior trim bonding.

Exterior mounting tapes and double-sided foam tapes are used to permanently attach side body moldings and emblems. This is a semistructural application that requires very high peel strength, excellent adhesion to automotive paint systems, and very high shear or cohesive strength, even at elevated temperatures. Since automobiles are expected to last a long time, adhesive performance must remain stable under outdoor weathering conditions. The adhesive must also have good chemical resistance to such substances as gasoline, salt spray, and detergent solutions.

Exterior graphic films are typically vinyl films for pinstriping, fleet markings, and other decorative applications. Good peel adhesion to automotive paints and sufficient shear (cohesive) strength to prevent wing-up or sag are required. The ability to remove the graphic film cleanly and reposition it at the time of application is desirable, yet the peel strength must build to a high level. The vinyl substrate challenges the adhesive to have excellent shrink properties and plasticizer resistance. Low or no color is desirable where white or light colored vinyls

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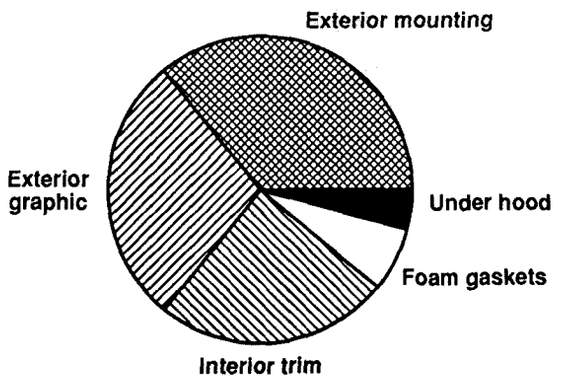
1. Acrylic PSA usage in the automotive market



I. Automotive market segments for acrylic PSA usage

Market segment	*Usage, %*	*Form*
Exterior foam mounting tape Side moldings Emblems	36	Primarily solvent
Exterior graphic films Pinstriping Fleet markings	28	Primarily solvent
Interior trim bonding Fabric bonding Carpet bonding Headliners Instrument displays, decals Watershields	25	Emulsion and solvent
Foam gaskets HVAC Sound deadening	7	Primarily emulsion
Under the hood Labels Sound deadening Gaskets	4	Primarily solvent
	100	

are used. Chemical resistance is important for the same reasons as in the exterior mounting tape application. Finally, other films besides vinyl can be used in these applications.

Interior trim bonding applications are also permanent bonding applications that require very high peel strength and good shear (cohesive) strength. Often the substrate material, such as cloth, foam, foam-backed cloth, or carpet, is adhered to low-energy surfaces, such as polyolefins. Typical automotive specifications require extensive cycle testing that involves high temperatures, high humidity, and low temperatures. Good peel adhesion under each cycle condition is required. Finally, good performance stability, as judged by weatherometer testing, is also necessary.

Acrylic PSA technology provides the wide latitude necessary to develop adhesives that satisfy this broad range of requirements.

II. Emerging applications for acrylic PSAs in the automotive market

Protective films (for shipping)
- Exterior
- Interior

Weather seal attachments
- Doors and rear hoods (trunks)

Under-the-hood applications
- Labels
- Decals

III. Performance requirements for exterior foam mounting tape

Adhesion (to BC/CC paints)
- 180°C peel
- Cleavage peel (90° peel)
- Pluck

Shear performance
- Room temperature
- Elevated temperature (70°C)

Stable performance (peel)
- 7 days at 70°C
- 1000–1500 hr weatherometer testing
- Florida and Arizona exposure
- Cycle testing
  - -30°C for 17 hr
    38°C, 100% RH for 24 hr
  - -30°C for 7 hr
    38°C, 100% RH for 17 hr
    80°C for 72 hr
    38°C, 100% RH for 24 hr

Chemical resistance
- Gasoline
- Mineral spirits
- Salt spray
- Detergent solution

Acrylic PSA technologies

Polymer chemistry

Typical acrylic PSA polymers are composed of a mixture of three or more monomers: a primary soft acrylic monomer or monomers with a low glass transition temperature (T_g), a hard or high T_g monomer or monomers, and one or more functional monomers. Examples are shown in **Table VI**. The functional monomers are present for several purposes, including cross-linking and increasing polarity. The combination of high and low T_g monomers influences the overall T_g and modulus of the polymer. The number of combinations and permutations of monomers that are possible provides the potential for a wide range of adhesive performance.

Molecular weight and molecular weight distribution of the polymer, which can be manipulated with chain

IV. Performance requirements for exterior vinyl graphic film

- Adhesion (BC/CC paint)
  - 180°C peel
  - Repositionability
    - Adhesion vs. time
      (1 min, 20 min, 7 days)
- Shear performance
- Tack
- Plasticizer resistance
  - 7 days at 70°C
  - Shrink resistance
- Low color
- Chemical resistance
  - Gasoline
  - Mineral spirits
  - Salt spray
  - Detergent solution

V. Performance requirements for interior trim

- Adhesion
  - Flexible substrates (cloth and foam-based cloth)
  - Adhesion to polyolefins
- Shear performance
  - No edge lift
- Environmental performance
  - Cycle testing
    - 38°C, 100% RH for 24 hr
    - 82°C for 4 hr
    - 82°C for 14 hr
    - 70°C for 168 hr
    - -30°C for 4 hr
    - 70°C for 100 hr
- Stable performance
  - Weatherometer testing
  - Plasticizer resistance

VI. Typical monomers and mixture amounts for acrylic PSA polymers

Soft (low T_g) 50-99%	*Hard (high T_g)* 0-30%	*Functional,* 0.5-15%
Ethyl-hexyl-acrylate	Methyl acrylate	Acrylic acid
Butyl acrylate	Methyl methacrylate	Hydroxyethyl acrylate
Octyl acrylate		Vinyl acetate
		Glycidal methacrylate
		N-methyl acrylamide

transfer agents and process conditions, provide other significant variables to modify adhesive performance.

To achieve high shear strength, cross-linking the polymer is necessary. In typical solution acrylic systems, this is done during drying by using metal chelate cross-linking (*1*) or amino cross-linking through hydroxy or acid monomer functionality. In emulsion systems, cross-linking can be done during the polymerization or during drying by approaches similar to that used in solution acrylics. Thermal cure through epoxy functionality is also sometimes used. Cross-linking improves shear performance but typically reduces peel and tack performance.

More recent emerging acrylic polymer technology includes cross-linking initiated by UV or electron beam. This method offers the possibility of altering the cross-linking density independently from the polymer T_g and polarity. It can also result in different flexibility of the cross-links. Another possible polymer technology, described by DuPont in 1989 (*2*), involves two-phase acrylic polymer systems to make a hot-melt acrylic PSA. The concept of two-phase systems can be extended in many directions, including to emulsion acrylic systems.

This brief summary of current and emerging acrylic PSA polymer technology just touches the surface of the possibilities. We are certain that these and other monomers (acrylic or otherwise), other polymer functionality, cross-linking chemistries, and a myriad of possible two-phase polymer structures could be utilized to make further breakthroughs in adhesive performance.

Formulation technology

In addition to modifications of the acrylic polymer, formulation of the adhesive is becoming another very important aspect of acrylic PSA technology. The use of tackifiers and plasticizers in acrylic systems has been found to be effective to improve certain performance properties. Tackifier may be a misnomer for acrylic systems. Sometimes "tackifiers" actually reduce tack, but they can increase peel, improve adhesion to low energy surfaces, and reduce viscosity of solution systems. Rosin ester tackifiers might reduce UV or thermal stability to a degree, but other hydrocarbon tackifiers and improved rosin tackifiers are being developed for acrylic systems.

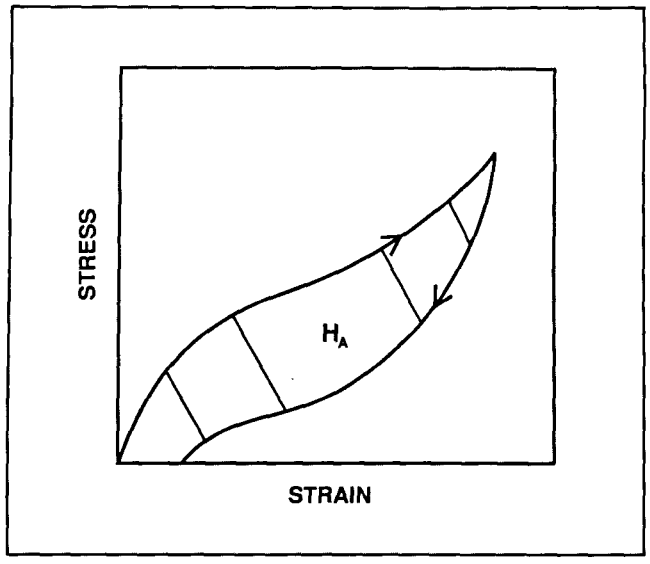
Other formulation routes to enhanced performance probably are being used or have not been tried yet. A discrete phase of organic or inorganic fillers as spheres or fibers could be used to increase the modulus and thus shear strength of the adhesive, especially if they were surface modified or chemically bound to the adhesive. This formulation route might improve shear strength without sacrificing peel or tack.

New product development methodology

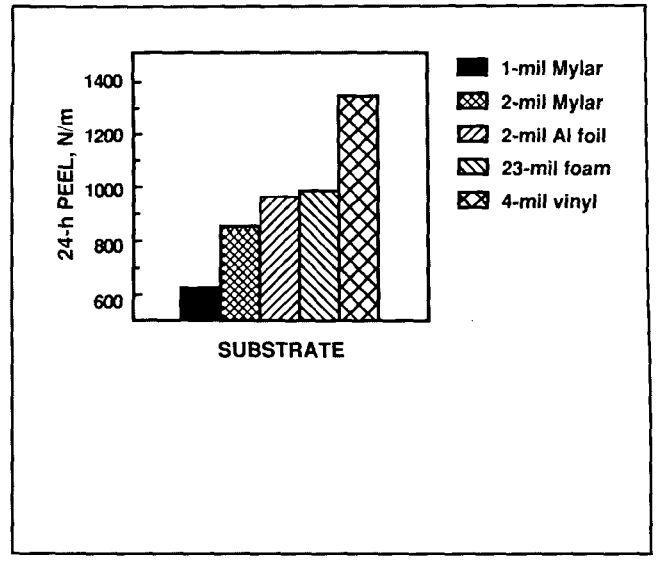
Experimental design techniques

The use of experimental design techniques for the development of improved acrylic PSAs has become an important tool for the polymer chemist (*3*). This enables optimization of performance properties in a very efficient manner. It is well suited to automotive applications, where the balance of properties is demanding and where many requirements must be met at the same time. It also permits the rapid screening of new chemistries and concepts.

2. Bulk energy dissipated by the adhesive



3. Effect of backing on peel performance for 1.5-mil solution acrylic PSA



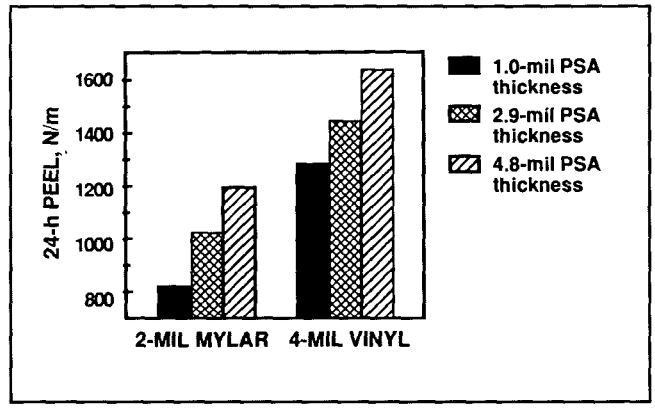
Cooperative supplier-customer efforts

Emerging needs from the automotive marketplace will continue to be the driving force for new adhesive development. The challenging nature of the adhesive performance requirements makes cooperative efforts between the adhesive supplier and the customer a key to success. Experimental design techniques and the use of a total system approach are powerful tools for these cooperative programs. Experimental design can greatly accelerate the product development effort. A total system approach can solve problems that the adhesive alone can not resolve. The cooperative effort is most successful when both parties view it as a true joint research and development program where both companies apply all of their scientific knowledge to the problem together.

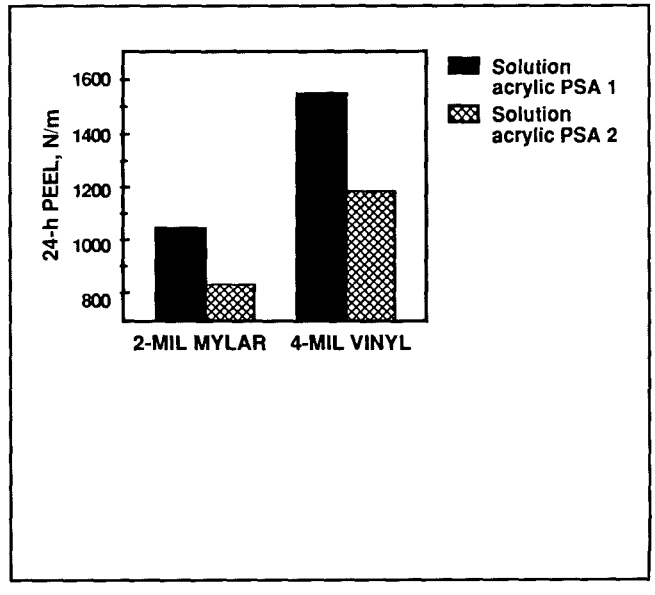
The application of material science to PSA technology is not new but is now sufficiently developed and acknowledged to be truly useful in new product development. The relationships between dynamic mechanical properties, mechanical properties, and PSA performance are now well enough understood to use these measurements to help design new polymer structures (*4*). The mechanics of energy dissipation in a peel test and tack test are also becoming better understood (*5, 6*). This understanding can be combined with measurements of the mechanical properties of the PSA to develop better adhesives.

These same concepts of material science can be applied to the structure of the total system to develop improved performance, as shown in the following discussion.

4. Effect of PSA thickness on peel performance



5. Effect of two different 1.5-mil PSAs on peel performance



Peel energy

The peel force measured in a peel test can be expressed by the following equation (*5*):

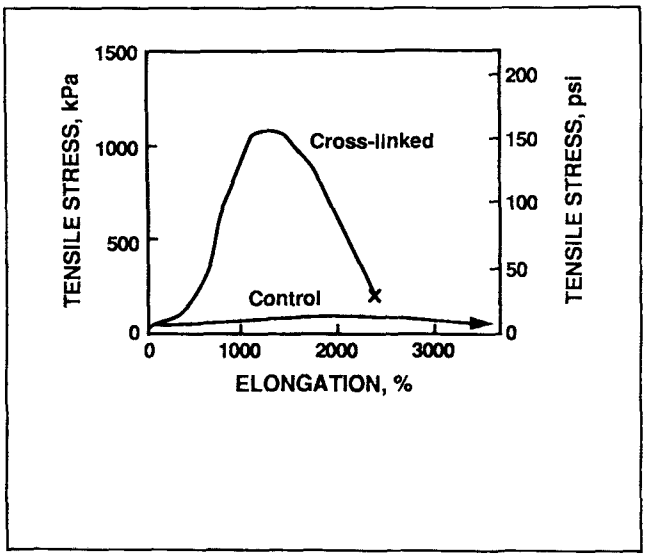
$$P = S + H_A + H_B + E$$

where

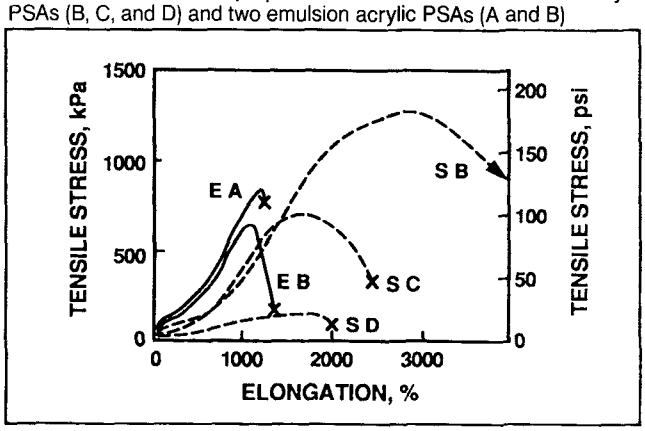
P = peel force

S = surface energy expended to create free fracture surfaces

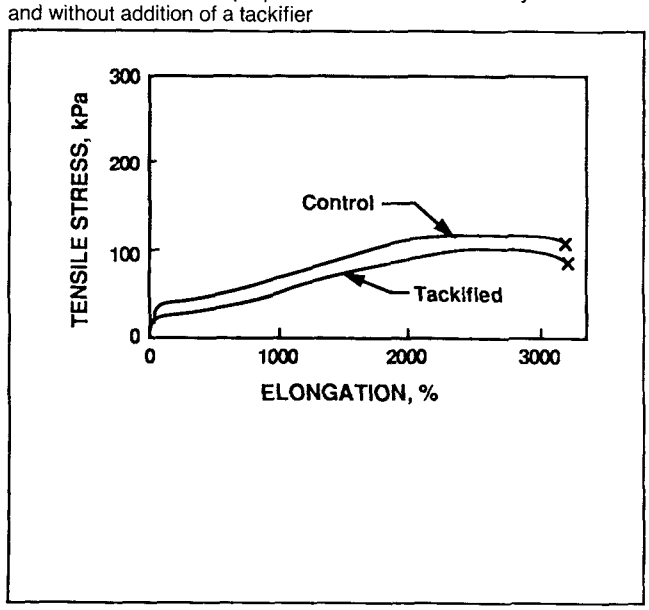
6. Tensile stress-strain properties of one solution acrylic PSA with and without addition of a cross-linker



7. Tensile stress-strain properties of three selected solution acrylic PSAs (B, C, and D) and two emulsion acrylic PSAs (A and B)



8. Tensile stress-strain properties of one emulsion acrylic PSA with and without addition of a tackifier



H_A = bulk energy dissipated within the bulk adhesive

H_B = bulk energy dissipated within the backing

E = strain energy within the new detached strip.

Typically the surface energy contributions are much smaller than H_A and H_B (*5*). In many instances, as for polyester, the backing is flexible but rather inextensible, so that the strain energy term, E, is often negligible. This may not be the case for a foam backing, however, where E might contribute significantly to the peel force.

The bulk energy dissipated by the adhesive can be depicted as shown in **Fig. 2** (*5*). As the peel test proceeds, the adhesive will experience a cycle of stress (extension) from zero to some maximum, where either cohesive or interfacial failure occurs, and then back to zero again (retraction). The energy lost is the area under the hysteresis loop, H_A. Similarly, the backing material experiences the same cycle, resulting in an energy loss H_B. Depending on the nature of the backing, its rigidity, and its thickness, H_B might be small, significant, or even greater than H_A.

This concept is clearly shown in **Figs. 3-5.** In Fig. 3, one acrylic PSA has been coated at the same coatweight on several different backings. As is evident, some of the thicker and more compliant backings make a significant contribution to the peel force. Figure 4 shows that by increasing the adhesive coating weight, the peel can also be increased. This is simply explained by recognizing that the energy dissipated will be proportional to the volume of adhesive undergoing the extension-relaxation cycle, provided the failure mode does not change. Finally, Fig. 5 demonstrates that the mechanical property differences of two different adhesives, as expected, change the peel energy as well.

Adhesive mechanical properties

We have been able to study the mechanical properties of acrylic PSAs using two different techniques (*4*). The first technique involves casting tensile bars from the PSA and running direct stress-strain measurements. Typical results of these measurements are shown in **Figs. 6-8.** The analysis is very similar to that shown in Fig. 2, except that there is no relaxation cycle. Figure 6 shows stress-strain curves for a relatively soft (cohesively weak) acrylic solution PSA with low cross-linking and a more cohesively strong acrylic solution PSA with a higher level of cross-linking. Both have the potential for a very high level of extension prior to fracture, but the larger area under the more cross-linked PSA will result in much greater energy dissipation and a higher peel strength.

Figure 7 compares three "typical" solution acrylic PSAs with two emulsion acrylic PSAs. At least in these cases, the emulsion PSAs showed similar ultimate strength (peak tensile strength) or cohesive strength. However, the emulsions extended less prior to fracture, compared with the solution PSAs. One might hypothesize that these emulsions would have lower peel values at equivalent shear values. This is indeed the case with the adhesives shown here.

Figure 8 shows the impact of one rosin ester tackifier on the stress-strain curve of an emulsion acrylic PSA. In

this case, the tackifier marginally reduces the tensile strength of the PSA and is evident in a somewhat lower shear strength.

The second technique involves casting small discs from the PSA and using a Polymers Laboratory DMTA (dynamic mechanical thermal analysis) unit to measure dynamic mechanical properties. **Figures 9-11** show the dynamic mechanical properties of the same adhesives shown in Figs. 5-8. Due to the large differences in frequency or test rate, and strain between the tensile testing and DMTA testing, we have found that high temperature (127°C) G′ values in the DMTA tests correlate with the peak tensile values (strength) in the tensile testing. From our work, it also appears that the PSA extensibility in tensile testing at least partially correlates with Tan δ at high temperatures (127°C) as measured under these DMTA conditions. However, this relationship is more complex.

In any event, large values of G′ and peak tensile strength by these measurements correlate well with PSA shear performance. Large areas under the tensile stress strain curves or high values of Tan δ correlate well with high peel values. These relationships fit well with the premise that energy dissipation within the adhesive (and backing) governs peel, and cohesive strength or modulus governs shear values.

Unfortunately, the rate of extension during peel testing is much greater than that during tensile testing, and the degree of extension during peel testing is much greater than the strains imposed during DMTA testing. Nonetheless, we are finding these direct mechanical property measurements very useful in the design of new adhesive systems. Once the correct temperature, frequency, and strain level superpositions are more quantitatively determined and applied, these concepts will be of even greater value.

Conclusions

The use of acrylic PSAs in automotive applications is significant. The applications are demanding and are based on the excellent UV and thermal stability offered by acrylic systems. Expansion of the use of acrylic PSAs, beyond simply market growth, will require advances in acrylic PSA performance for new applications. The myriad of possible polymer chemistries both old and new, improved methodologies including experimental design, cooperative supplier-customer programs, material science approaches, and total system approaches makes those advancements possible.□

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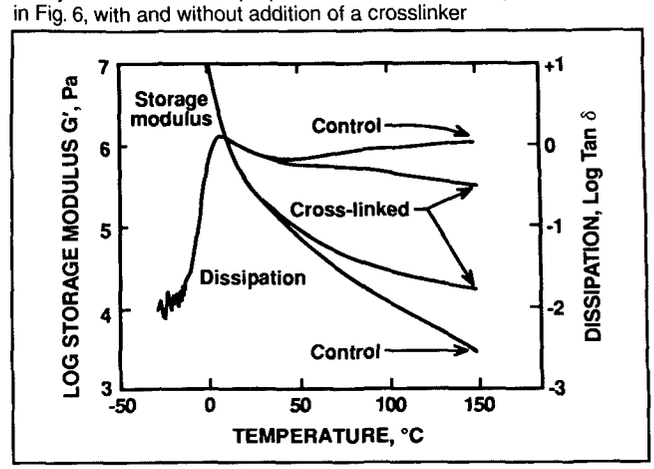
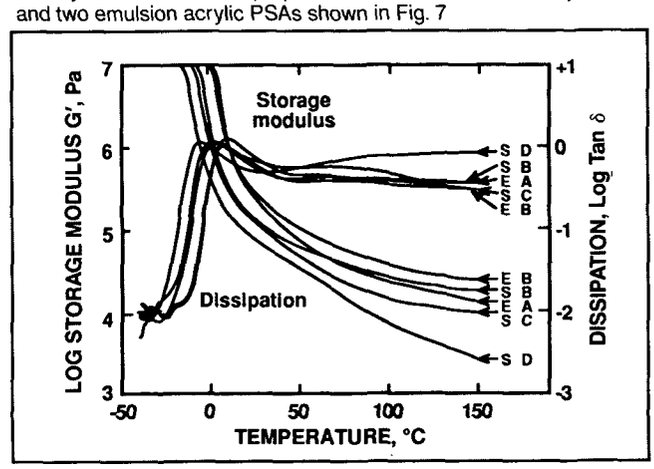
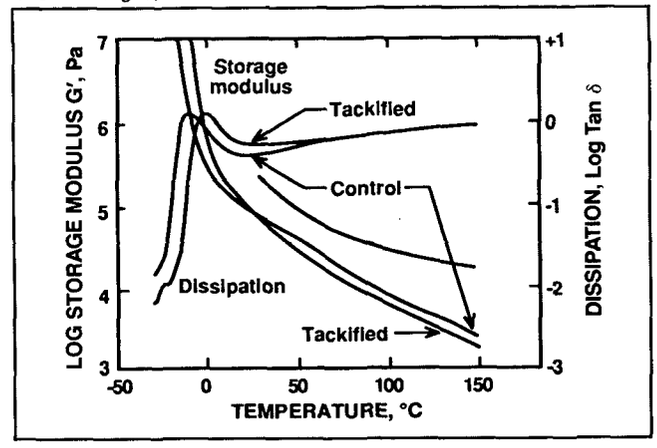
9. Dynamic mechanical properties of the solution acrylic PSA shown in Fig. 6, with and without addition of a crosslinker



10. Dynamic mechanical properties of the three solution acrylic PSAs and two emulsion acrylic PSAs shown in Fig. 7



11. Dynamic mechanical properties of the emulsion acrylic PSA shown in Fig. 8, with and without addition of a tackifier



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