

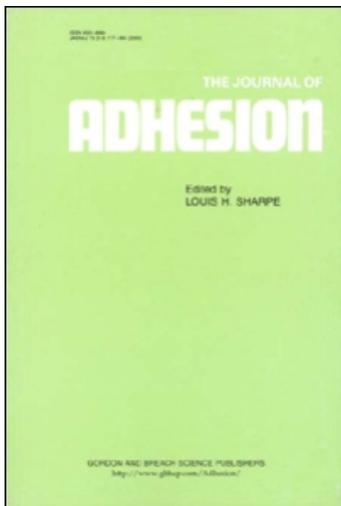
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Mechanical Properties of Acrylic Pressure Sensitive Adhesives and Their Relationships to Industry Standard Testing

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Mechanical Properties of Acrylic Pressure Sensitive Adhesives and Their Relationships to Industry Standard Testing

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Dynamic mechanical and tensile stress-strain properties were measured for four sets of acrylic pressure sensitive adhesives, and were compared to industry standard “applications” peel and shear properties. Correlations were established showing that more than half of the range of performance shown by commercial PSA’s is controlled by the bulk mechanical properties of the adhesive polymer. A few exceptions stand out clearly. Also, room temperature performance properties were found to correlate better with DMA at higher temperatures than with room temperature DMA. The contribution of tensile properties to peel strength and failure mode is discussed. The results can be used to relate PSA performance to well-known concepts in other areas of materials science, *e.g.* fracture toughness, rubber elasticity, and rheology, and to key variables in the adhesive formulation or selection process.

KEY WORDS Pressure sensitive adhesives; acrylic PSA’s; dynamic mechanical analysis; viscoelasticity; tensile tests; performance; peel strength; shear strength; creep; modulus.

INTRODUCTION

It is well recognized in general terms that both surface forces and bulk viscoelastic behavior play critical roles in the performance of pressure sensitive adhesive (PSA) products and bonds,^{1,2} even though their relative importance in a particular application and the details of the interplay between them are still objects of active study. This paper considers some measurement techniques for bulk mechanical properties of acrylic pressure sensitive adhesives, and their relationships to the performance of adhesive bonds as measured by industry standard test methods. It is hoped that greater use of such characterization will contribute to basing product development on a stronger understanding of basic materials properties and molecular mechanisms.

Tensile properties are used almost universally on structural materials including

adhesives, but have seldom been reported for PSA's³⁻⁵ Butt joints, lap shears, and other methods have provided some indirect assessments, frequently complicated by edge effects from the substrates. Therefore, we considered it preferable to measure the tensile properties as directly as possible, to isolate the basic properties of the bulk adhesive itself. Use of the dynamic mechanical (DMA) approach to viscoelastic properties is well established for polymers in general, and is becoming more widely used for PSA's^{6,7} More recent investigations have started to focus on specific differences between materials, often showing only pairwise comparison of two adhesives.⁸⁻¹⁰

One purpose of this paper is to develop further the general concept that performance of successful PSA's requires materials that simultaneously possess both solid-like strength and liquid-like flow behavior. Viscoelastic properties in particular arise from the amount and types of chain mobility or restraint present, and may reflect polymer structure from the atomic level (chain composition), to gross morphology (crystallinity, crosslinking or gelation). Control of chain mobility is of obvious importance in obtaining the desired degree of bond formation (tack, completeness of wetting) and bond release (strength, failure mode, residue) for a particular application.

EXPERIMENTAL

Bulk adhesive samples suitable for mechanical testing were prepared by casting the liquid adhesive into smooth flat films about 0.040 inch thick. With proper control of the atmosphere, emulsions dried unaided to a constant weight in a few days, but solutions were vacuum-dried in the final stage. Well-dried films gave off no further trappable volatiles after a week or more of further vacuum drying. The castings were held between release papers, frozen briefly to simplify handling, then die-cut to the desired shape. Tensile tests were done on standard ASTM (D-1822, Type L) dumbbell-shaped specimens, 2 inches long with a gage section 3/4 by 1/8 inch. Samples were conditioned at 22°C and 50% RH for at least 24 hours before tensile testing at 5 inches/minute. For such highly extensible materials, the tab portion of the specimen had to be gripped tightly in the test machine to prevent its pulling out. Some materials extended without breaking to the full 36 inches of travel available on the machine.

Dynamic mechanical methods and their physical interpretation for polymers in general are given in several textbooks, e.g.,^{11,12} and only a brief summary will be given here. Disks 3/8 inch in diameter were cut from the thick films and sandwiched between aluminum plates in a shear geometry in a Polymer Laboratories Dynamic Mechanical Thermal Analyser (DMTA). To assure adhesion at all temperatures used, the shear gap was fixed at room temperature to be 15% thinner than the free thickness of the specimen (and it was verified that small amounts of compression had very little effect on the results). The storage modulus and $\tan \delta$ at 1 Hz and an imposed shear strain $\gamma \cong 0.06$ were scanned at 5°C/minute over the temperature range from -50 to +150°C, averaging four to

six readings during each 1°C interval. The scale used here for dissipation (\log of $\tan \delta$) has the convenience that a numerical value of zero represents an even balance between liquid-like and solid-like properties, and indeed has been proposed¹³ to represent the gel point. Positive values of $\log \tan \delta$ then represent more liquid-like viscous behavior, and negative values more solid-like elastic behavior.

Four sets of acrylic pressure sensitive adhesives are presented here. The most straightforward was a laboratory model system (XLQ) where a single linear solution multipolymer was formulated using varying amounts of a proprietary crosslinking system, ranging from zero to well in excess of optimum. An emulsion process design study (EPS) provided samples made from a single monomer recipe, differing only in polymerization conditions. Also, two "families" representing the wide range and balance of properties available for specific applications were selected from the commercial Monsanto Gelva[®] Multipolymer Emulsion (GME) and Solution (GMS) product lines. The commercial GME and GMS samples included two tackified adhesives and their base polymers, one plasticized adhesive, a low-temperature adhesive, and one removable, as well as examples of high peel, high shear, and balances of properties. For each set, tensile, dynamic mechanical, and applications properties were measured in duplicate or better. Applications properties were measured after conditioning at standard conditions of 22°C and 50% RH, using a 1 mil adhesive film on a 1 mil Mylar[®] backing from stainless steel panels. Peel was done at a 180° angle and at 12 inches/minute by PSTC Method 1 and shear by PSTC-7 using a one-pound weight hanging from a 1/2 by 1/2 inch joint (quarter-square-inch, or qsi) for the emulsions, and one kilogram/qsi for the solutions.

RESULTS AND DISCUSSION

Tensile test results of PSA's showed a remarkably wide range of behavior and, since we have seen no complete curves published before,³⁻⁵ we present some details. Two typical curves are shown in Figure 1. Note that the scales go to less than 300 psi in strength, but to more than 3600% in extension, confirming that PSA's are much softer and more deformable than other types of commercially-used polymers, even the softest rubbers. The shape of the curves usually showed two distinct phenomena. After an initial steep rise from zero extension, there was a knee or folding over around 100% extension, after which the curve often rose again to a peak around 1000–2000%. The declining side of the load peak appeared stable, and was not accompanied by visible tearing or stress-whitening of the specimen, which stayed transparent throughout. When the sample broke during the test, failure was by tearing in the central portion of the sample which propagated across the width in a few seconds (smaller than the "X" which marks failure in the curve). We believe that these load features are associated with flow of individual chains, and with flow or tearing of the crosslink structure, respectively. From the curves, we took the maximum strength (regardless of its location along the curve) and the maximum extension as the two points of

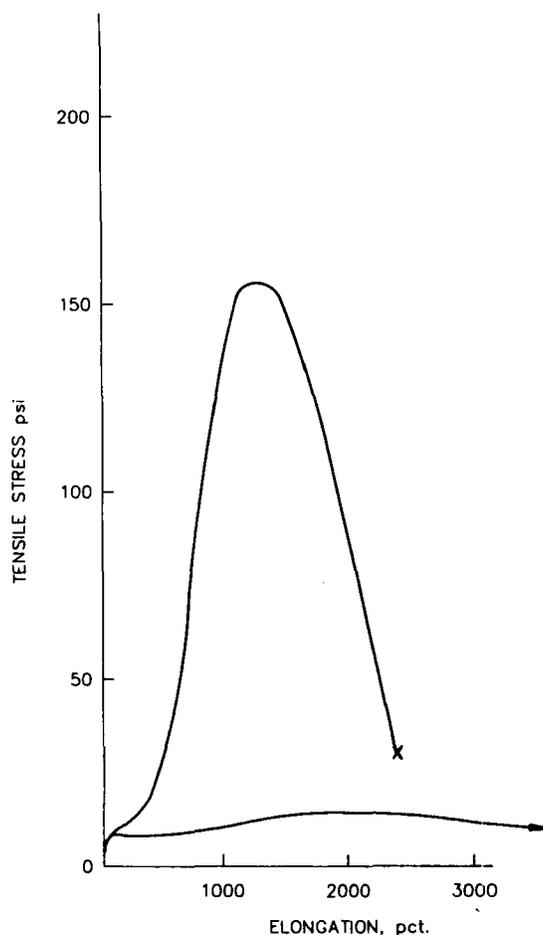


FIGURE 1 Tensile test results of two typical acrylic pressure sensitive adhesives.

greatest interest, but it is likely that there is also valid information in some of the other features. It is also of interest that tensile curves of block copolymer PSA's obtained independently⁵ also showed a similar knee in the initial portion near 100%, and the rising side of what may be a major peak; hysteresis measurements in that case confirmed that the feature near 100% was indeed a yield point.

Typical dynamic mechanical spectra of two PSA's are shown in Figure 2. The dominant feature is the glass transition, T_g . Below this transition, the materials are glassy, and would show no useful pressure sensitive adhesive properties. Above T_g , the materials show liquid-like or rubbery behaviour, and acquire the characteristics of PSA's. The storage modulus decreases slowly with temperature, while the dissipation, which is consistently much higher in PSA's than in engineering polymers, may stay relatively low, or may rise slowly with temperature.

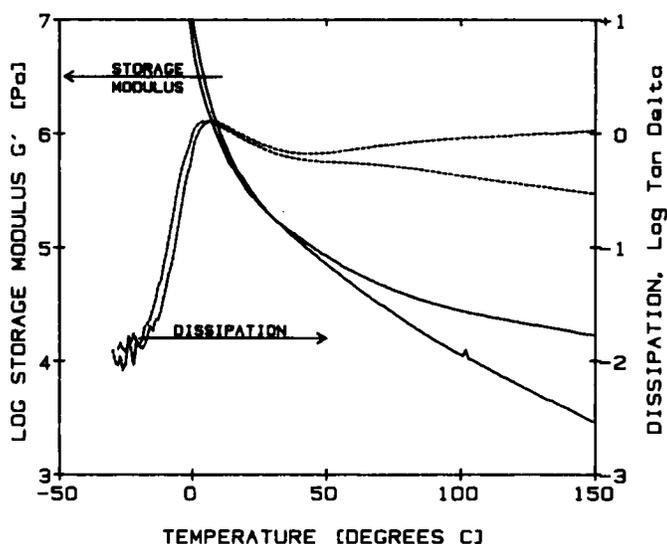


FIGURE 2 Dynamic mechanical spectra of two typical acrylic PSA's.

For many other classes of materials, the temperature and intensity of such transitions are the most important results of DMA. However, our results on many acrylic PSA's have shown T_g at 1 Hz to be consistently within a few degrees of 0°C , and to show little correlation with room temperature performance properties (within the limits of commercial PSA's). In this regard, it will be noted that these acrylics offer a benefit for interpretation of structure-property relationships, not complicated by systematic shifts in T_g inherent in other PSA technologies. In the present materials, we noted that even when there were major differences in room temperature performance properties, the spectra were quite similar at lower temperatures. Only at temperatures above about 50°C did the curves start to diverge, and differences among materials became clear. For this reason, values of storage modulus and dissipation at the relatively high temperature of 127°C (400°K for rubber elasticity calculations) were selected to summarize the spectrum as a single point, as discussed later. It was recognized that the time scales of the mechanical experiments were not close to those of either peel or shear, but it will be seen that the results are useful nevertheless.

We turn now to the dependence of mechanical properties on the formulation of the adhesive. Figure 3 shows the tensile test results from the crosslinker model system, from which the previous "typical" curves were taken, where the number on each curve is an index representing the relative amount of crosslinker. The most striking feature is the extreme range of strength and elongation caused by varying the crosslinker level. The strength increases by a factor of about 40, from less than 5 psi to over 200, as crosslinker is added. The extension falls by a factor of at least two, although half the samples run offscale. The curves also show graphically how the deformation behavior changes from liquid-like, highly extensible flow with low strength to solid-like tearing with higher strength as the

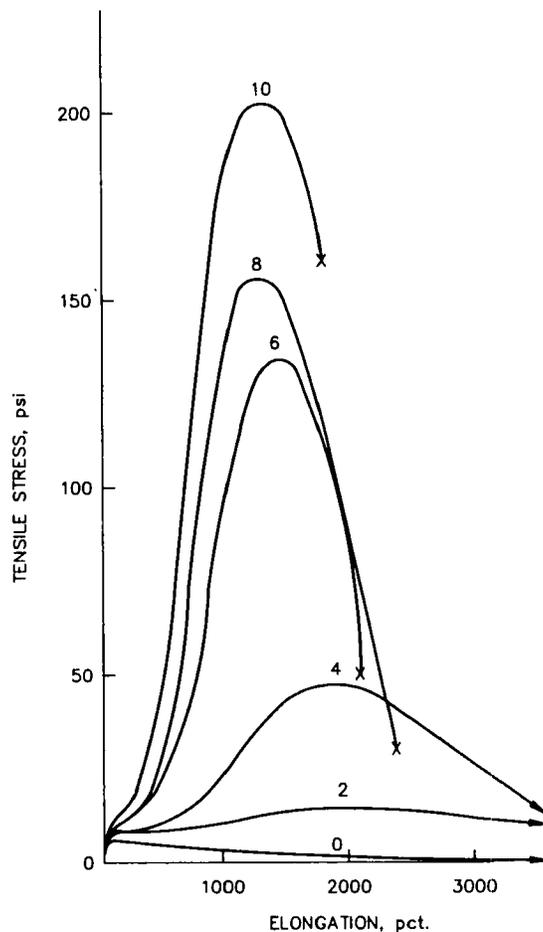


FIGURE 3 Tensile test results for a series of six levels of crosslinker in a solution PSA.

crosslink network increases. The corresponding dynamic mechanical spectra are shown in Figure 4. There are no significant differences below about 50°C, but the effect of adding crosslinker is to cause a large increase in the storage modulus at elevated temperature, by more than a factor of 10. The high-temperature dissipation decreases by nearly a factor of 10, corresponding to a change from liquid-dominated deformation behavior without crosslinker (and runs offscale again), to relatively solid-like behavior at the higher levels. Although the changes in DMA properties are not as dramatic as for the tensile tests, recall that they are being observed at a much smaller strain of about 6% *vs.* thousands of percent for tensiles, in an essentially nondestructive test.

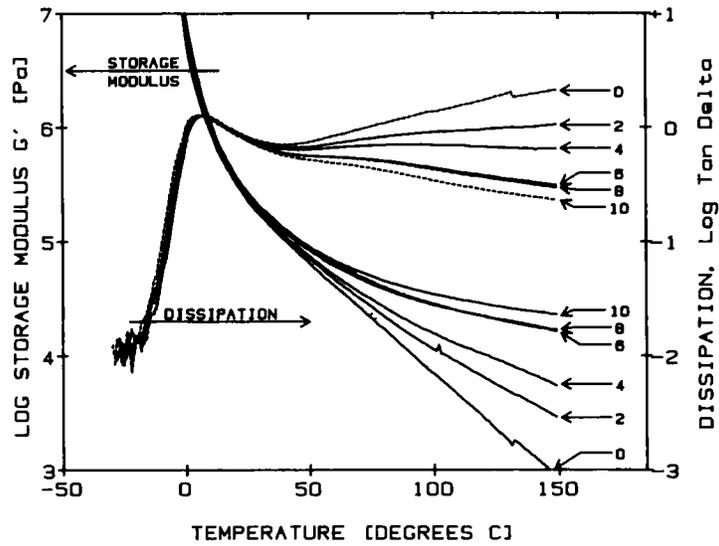


FIGURE 4 Dynamic mechanical spectra for the series of six crosslinker levels in a solution PSA.

RELATION OF MECHANICAL PROPERTIES TO STANDARD APPLICATIONS TESTS

Figure 5 shows an example of the relationship between an application property and a basic mechanical one, here peel at 20-minute bond dwell time and log tan δ , for the same cross-linker series. The peel strength (in pounds per linear

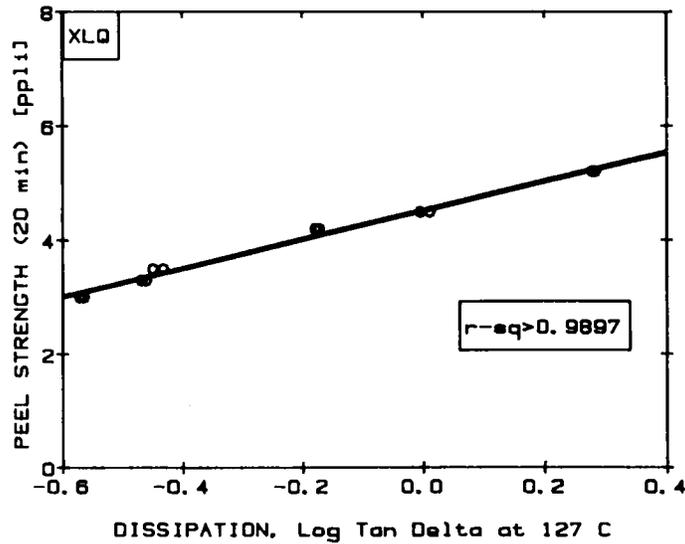


FIGURE 5 20-minute peel strength vs. log tan δ at 127°C for the crosslinker series, ($r^2 > 0.9897$).

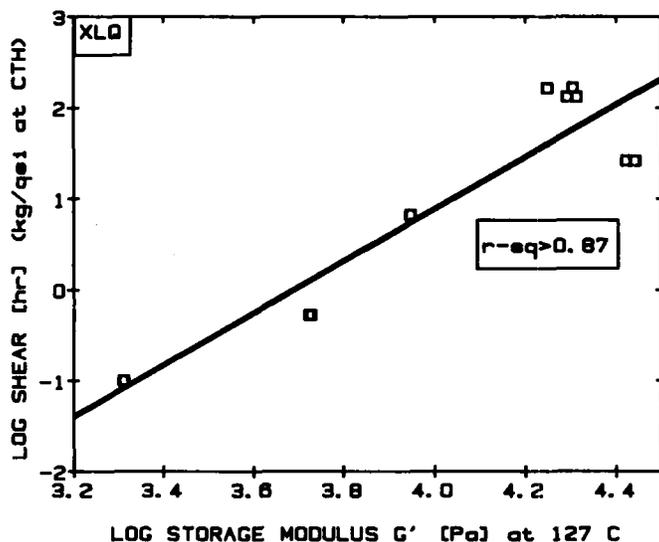


FIGURE 6 Log of Shear hang time (1 kg/qsi) vs. log storage modulus at 127°C for the crosslinker series, ($r^2 > 0.87$).

inch width, or ppli) was measured for each formulation and plotted against the dissipation at 127°C taken from the DMTA curve, and a straight line was fit. The goodness of fit of this correlation as measured by r^2 is greater than 98%. Figure 6 shows a similar relation between log shear (expressed as hang time or so-called shear strength) and log storage modulus at 127°C for the same materials. Both properties increase dramatically with crosslinker, and r^2 is 87%.

It is not surprising that applications properties are related to the viscoelastic behavior of the adhesive, and Figures 5 and 6 demonstrate this more clearly and quantitatively than usual. However, it was surprising that the better measure of viscoelastic behavior was the dissipation at some higher temperature, rather than at use temperature. We suspect that this was because the DMA data were taken at relatively small strains, while the decisive energy dissipation in peel is that at higher strains, more like those seen in the tensile tests. Dahlquist has reported measured boundary strains during peel on the order of 10 (1000%) for acrylic PSA's.¹⁴ Andrews specifically cautions against use of $\tan \delta$ as the measure of energy dissipation during peel because of this strain discrepancy,^{15,16} and we may have been fortunate in being able to stimulate high strains by using high temperatures. The Appendix discusses further the background¹⁷⁻²¹ and implications of the trade-off between high strains and high temperature.

We consider next a series of GMS commercial solution products selected to show the wide range and balance of performance properties needed to meet specific application requirements. In contrast to the idealized one-variable model above, the development of individual commercial adhesives of course uses strategies of monomer selection, polymerization conditions, molecular weight and its distribution, surfactants, crosslinkers and other additives, and other tools of

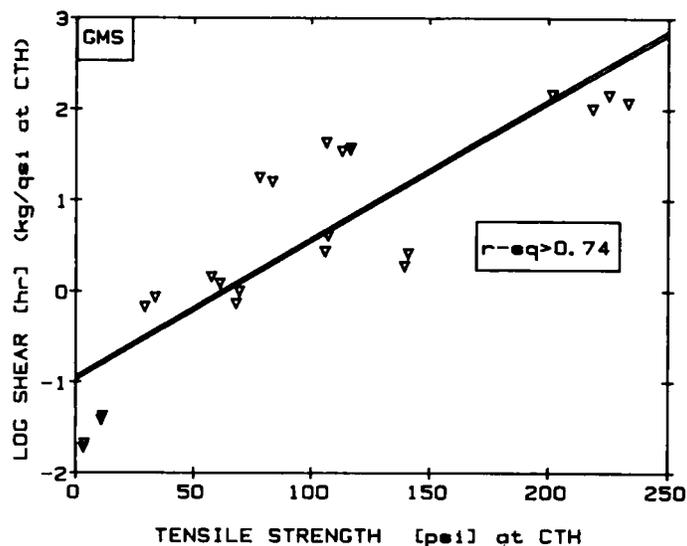


FIGURE 7 Log of Shear hang time vs. tensile strength for the GMS solution products, ($r^2 > 0.74$). CTH conditions are 22°C, 50% RH.

the chemist's craft to achieve the desired properties. Figure 7 shows the relationship between shear and tensile strength. The wide range of commercially-desirable properties is reflected in this figure, where the tensile strengths range from less than 4 psi to about 240 (about the same range shown by the crosslinker series), and shear covers nearly four decades of hang time. Still, tensile strength correlates 74% with the variation seen in shear. Figure 8 shows the relationship

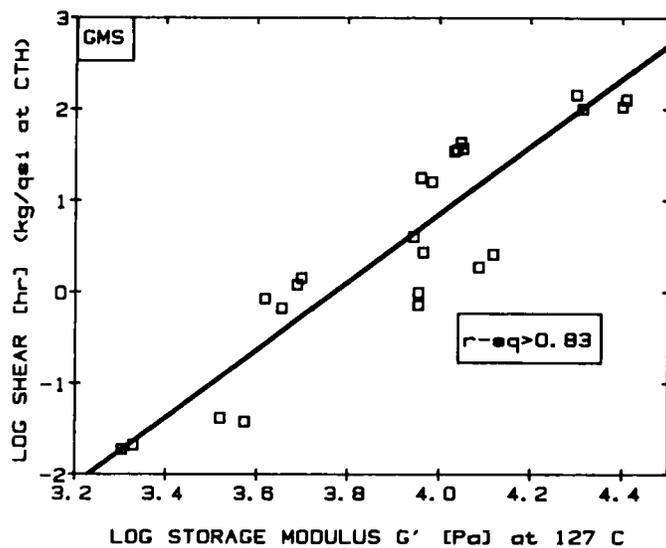


FIGURE 8 Log of Shear hang time vs. storage modulus for the GMS solution products, ($r^2 > 0.83$).

between log shear and high-temperature storage modulus, and the correlation is $r^2 > 83$. Shear is often considered to reflect the cohesive strength of the adhesive, and the data show that this can be assessed either directly from tensile tests or from the storage modulus of the dynamic test. Figure 9 shows the relation between 20-minute peel and dissipation for the solution products. Peel strength also covers a still-wider range here than that achieved by crosslinker alone, and flow behavior as measured by $\log \tan \delta$ correlates 53% with the observed variation in peel performance. Correlation of peel with tensile elongation also showed a positive result, but with lower r^2 ; one limitation on the quality of r^2 here was the range of elongations that could be measured.

We next consider emulsion adhesives, where the best "model" data were taken from a process design study where the monomer composition was essentially held constant, and properties were altered using process variables. Figure 10 shows the relation between log shear at 1 lb/qsi and storage modulus. Despite the quite different technologies used, it is seen that the emulsion and solution adhesives show fairly similar values for high-temperature modulus G' . Storage modulus correlates with 85% of the variation in shear. Tensile properties were not taken for this set. Figure 11 shows the peel strength at 20 minutes dwell *vs.* $\log \tan \delta$; again there was less range than in the previous series, and r^2 was 63%, with one outlying point accounting for most of the reduction. It is of interest that in this series, correlations between performance properties and viscoelastic ones were stronger than between performance and the input variables to the process, suggesting that the viscoelastic properties are a more basic underlying mechanism, and the process variables are means to this end.

We turn now to property relationships in the set of GME commercial emulsion

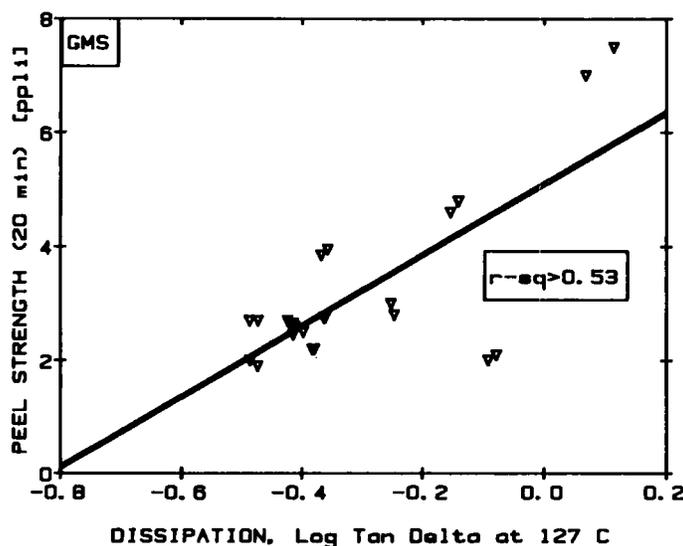


FIGURE 9 20-minute Peel strength *vs.* dissipation for the GMS solution products, ($r^2 > 0.53$).

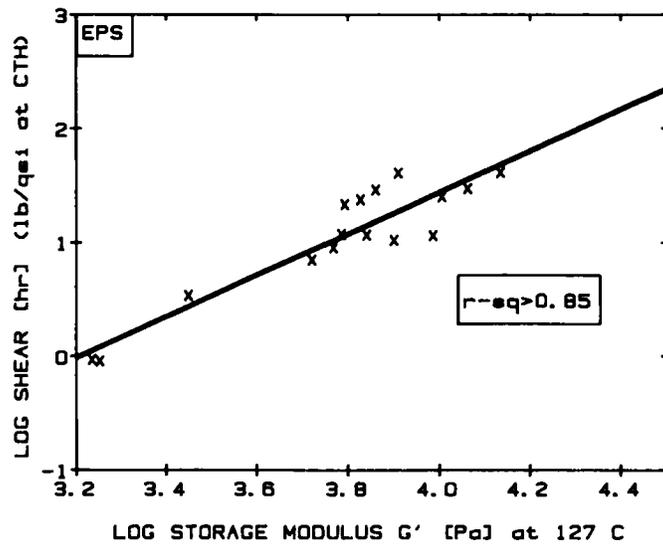


FIGURE 10 Log of Shear hang time vs. storage modulus for the emulsion process design series, ($r^2 > 0.85$).

adhesives. Figure 12 shows a similar correlation between 20-minute peel and dissipation, where $r^2 > 0.69$. Figure 13 shows the bulk tensile strength, and its relation to shear. Tensile strength runs from 10 to over 100 psi, and correlates 83% with the observed variation in shear. One material is plotted as a different symbol which falls far from the correlation line, and was excluded from the fit;

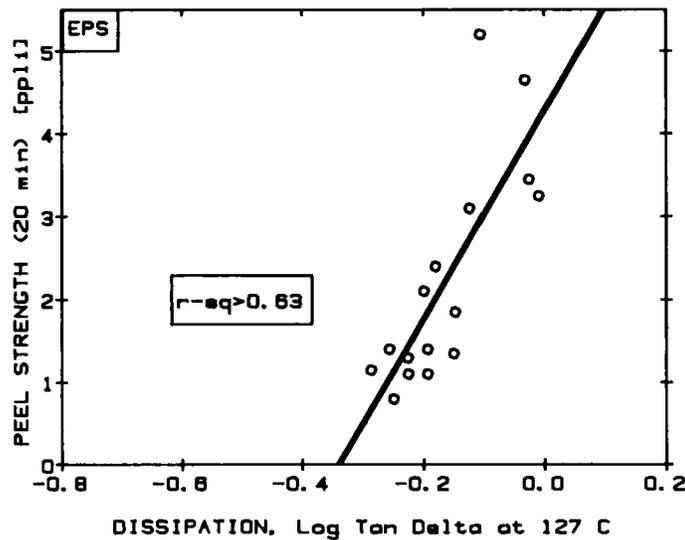


FIGURE 11 20-minute Peel strength vs. dissipation for the emulsion process design series, ($r^2 > 0.63$).

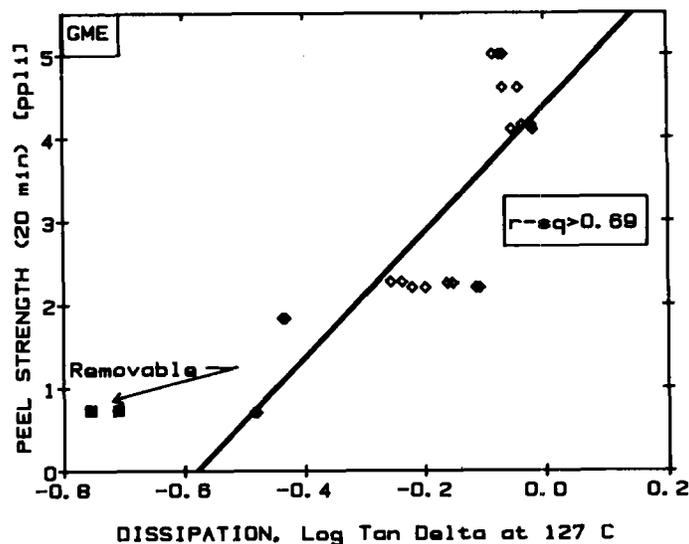


FIGURE 12 20-minute peel strength vs. $\log \tan \delta$ for the GME emulsion products, ($r^2 > 0.69$). The removable GME is excluded.

this point represents the only removable adhesive in these sample sets. Besides being an application with unusual performance requirements, removables are made by a unique and novel chemistry compared with the other products, and would not be expected to fit the same correlations. The removable is also marked separately in the peel behavior in Figure 12, where it also falls off the line, but

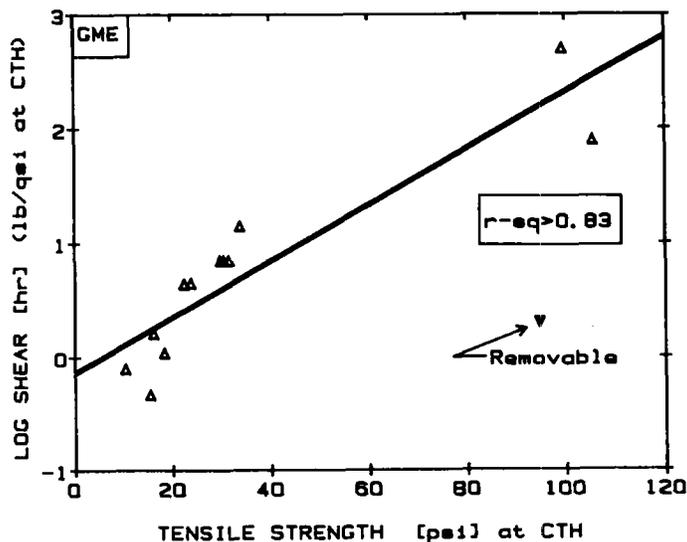


FIGURE 13 Log of Shear hang time (1 lb/qsi) vs. Tensile Strength for the GME emulsion products, ($r^2 > 0.83$). The removable GME is excluded.

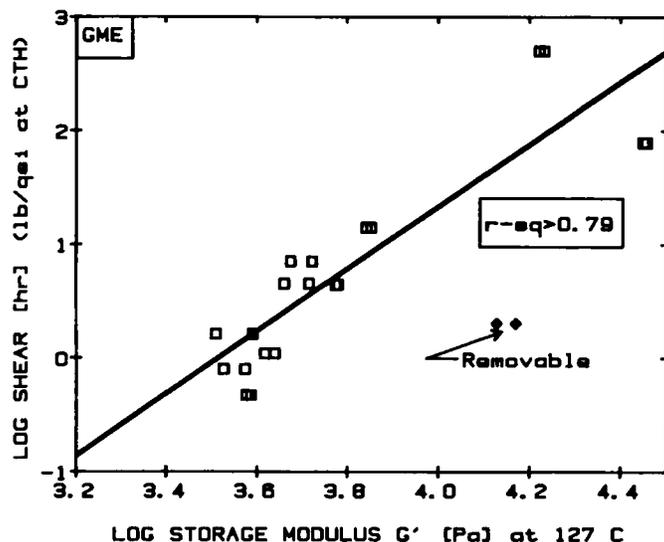


FIGURE 14 Log of Shear hang time (1lb/qsi) vs. log Storage modulus for the GME emulsion products, ($r^2 > 0.79$). The removable GME is excluded.

does not affect the correlation so much. Figure 14 shows a similar plot of shear vs. the storage modulus for the GME emulsion series, again with the removable excluded. The modulus covers nearly a decade in range, and r^2 is 79%. Again, high-temperature storage modulus and room temperature tensile strength showed equally good correlations with shear. In both the commercial solution and emulsion series, it appears that tailoring of PSA properties to the particular applications was done more through modification of bulk mechanical properties than through changes in surface adhesion.

Other data not shown here illustrate the limits of mechanical properties' control of performance. A separate solution process study included changes in monomer composition which resulted in significant variations in T_g and surface energy; here shear still correlated with G' at $r^2 > 0.64$, but peel correlated with $\tan \delta$ only after 24 hour bond dwell (*cf.* 20 minutes above), and then only at $r^2 > 0.22$. Such a result is still statistically distinct from zero ($p < 0.01$), but clearly of little predictive value. Because of the changes in T_g , 1-second probe tack here showed a strong negative correlation with room temperature storage modulus, $G'(22^\circ\text{C})$, confirming the Dahlquist criterion,²² or with T_g itself; but 24-hour peel showed this weakened version of the same positive correlation with high-temperature $\tan \delta$ seen in other sample sets. In another emulsion process study, where modifications were made by adjusting surfactant formulations, relations between bulk mechanical properties and performance vanished completely. We also noted that, in addition to the relations cited above, there were inter-relationships among laboratory properties, e.g. modulus and tensile strength, that were even stronger and more robust.

GENERAL DISCUSSION: ROLE OF TENSILE PROPERTIES IN THE PEEL TEST

Peel strength may be considered as an energy per unit area to separate the backing from a substrate, and is conceptually similar to other measures of fracture toughness of bulk materials. As a mechanical energy, peel is the product (or integral) of a force generated within a process zone, times a displacement to complete the separation process, either by adhesive failure at the interface,[†] or by cohesive failure of the bulk polymer. On the other hand, shear always involved cohesive failure, and is considered to reflect only the time-dependent cohesive strength of the adhesive.

Comparison of Figures 3 through 5 shows clearly that addition of crosslinker had the apparently paradoxical effect of greatly increasing the area under the stress-strain curves and increasing G' , while decreasing the adhesive peel strength. This agrees with experience, but is of particular interest in light of the diversity of models for peeling behavior. Some have assumed that peel strength is controlled by the failure strength (or energy) of the bulk polymer, or is proportional to the magnitude of G' , perhaps taken at a temperature somewhat above or below use temperature to account for the difference in rates. Many data examples are taken from rubber/resin systems where performance is modified by changes in composition which also cause changes in T_g . The XLQ data are at low enough crosslinker levels that there is negligible shift in the T_g , and while there is nothing special about that the choice of 127°C for the high-temperature modulus, Figure 4 shows clearly that no frequency- or temperature-shifting argument can alter the ranking of the six materials.

We emphasize that most of the peels reported here failed in the adhesive mode, including all of the crosslinker series and all but two of the GMS series. In this case the energy integral is not the complete curve as in Figure 3, but is truncated at some lower "boundary stress", σ_0 , corresponding to failure at the interface. Then the energy integral becomes that sketched in Curves 1 and 2 of Figure 15 where the boundary stress is taken as a constant. If the adhesive failure mode is indeed stress-limited as sketched, then the peel energy necessarily increases as the modulus decreases. This results in the trade-off relationship frequently observed between adhesive peel and shear, and different combinations of properties are desirable for different applications. Nearly the opposite applies in the less common case of cohesive peel. If the tensile stress never exceeds the boundary stress (Curve 3 of Figure 15), then the full stress-strain curve is utilized, and there is a well-known transition to cohesive failure and much higher peel strength. A schematic of the expected changes in peel strength and mode with tensile strength or modulus is sketched in Figure 16. In practice, the transition often shows a patchwork mixture of both modes, but in principle it is a

[†] "Adhesive" and "cohesive failure" are used here as in the PSA tape industry, to indicate whether or not a visible and tacky adhesive residue remains on the substrate. Regardless of the exact locus of failure, there is an unmistakable transition in both the peel energy and the visible distribution of the adhesive polymer.

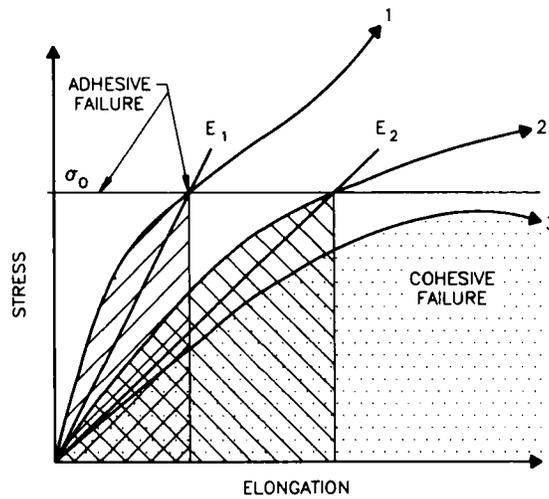


FIGURE 15 Schematic of the energy integral for adhesive and cohesive peel failure of adhesives of varying tensile strength.

discontinuity. In the cohesive mode, both shear and peel decrease if tensile strength and G' decrease still further.

The greatest number of cohesive peels (four of eleven) was found in the GME data, which show some support for the schematic. Figure 17 shows peel and mode *vs.* tensile strength, and it is seen that the cohesive failures had the highest peel strengths and lower average tensile strength. Peel increases with tensile strength

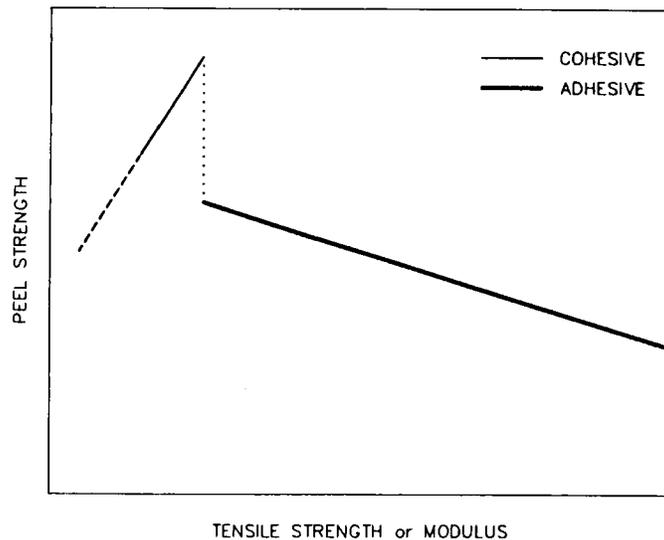


FIGURE 16 Schematic of the variation of peel strength and mode with tensile strength or modulus of the adhesive.

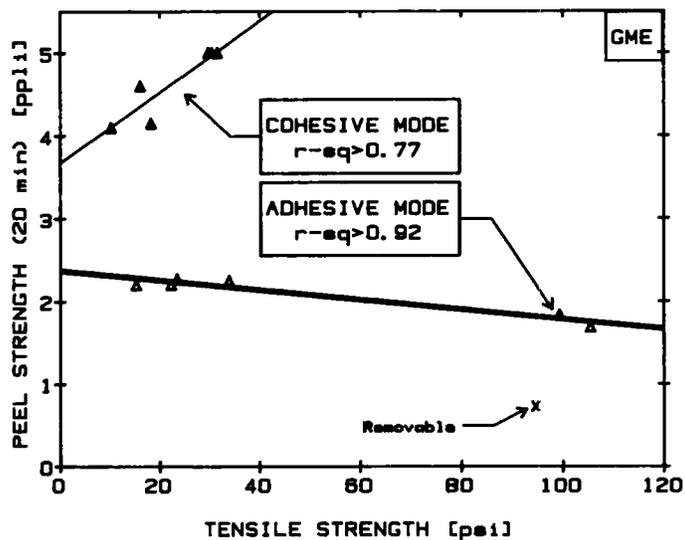


FIGURE 17 20-minute peel strength and mode *vs.* Tensile Strength for the GME emulsion products. The removable GME is excluded.

in the cohesive regime and decreases in the adhesive regime as expected. There is, however, some overlap in the cohesive and adhesive tensile strengths, probably because the boundary stress, σ_0 , is not as constant among these adhesives as Figure 15 suggests. Figure 18 shows that peel *vs.* high-temperature G' is very similar. The peel data also included two cohesive failures among the GMS's; they had the highest peel strengths and the lowest tensile strengths in that

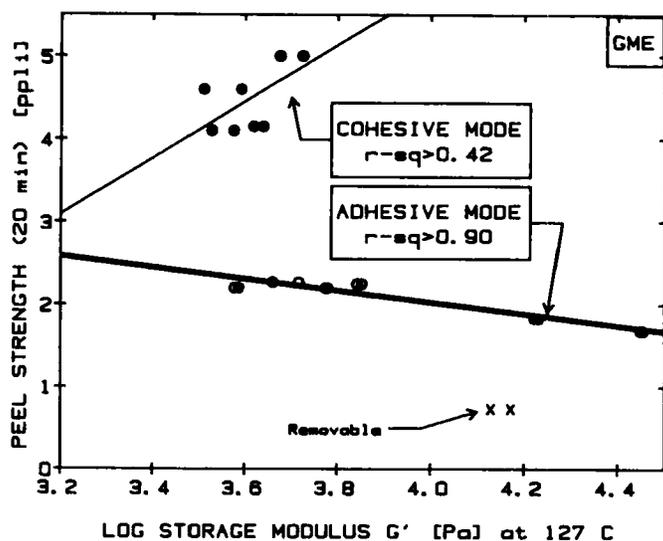


FIGURE 18 20-minute peel strength and mode *vs.* log Storage modulus for the GME emulsion products. The removable GME is excluded.

series, along with lowest G' and high $\tan \delta$ at 127°C. Clearly this combination of properties somewhat below the transition is desirable for certain applications, although at some sacrifice of shear. However, a material still farther below the transition loses both peel and shear, and would not be useful as a PSA. Similar changes in peel strength and mode have been presented by Druschke,²³ using an index of molecular weight as the independent variable. We also note previous suggestions of Kraus *et al.*⁶ and others, relating probe tack to a high value of G'' for resistance to viscous flow combined with a low G' for rapid surface contact (as originally proposed by Dahlquist).²² Although they referred to different temperatures than we have used, the concept is exactly equivalent to a high $\tan \delta$, and might also apply to peel. Gent and Hamed, e.g.,²⁴ have also discussed in some detail the role of energy dissipation in the peel of green rubber, relating it to room temperature tensile curves to Figure 15.

Bulk viscoelastic properties clearly account for much of the range of performance properties in both the commercial and selected laboratory examples shown above, and suggest that consistent physical principles underlie the performance, independent of the chemistry by which they are achieved. In agreement with others,^{1,16,25-28} we believe that surface adhesion serves primarily to prevent premature separation from the substrate as illustrated in Figure 15, and that flow and viscoelastic energy dissipation in the bulk adhesive account for the large excess (2 to 4 orders of magnitude) of observed peel energies over surface energy. Our results suggest that bulk properties dominate performance in about 3/4 of the observed cases.

CONCLUSIONS

Our results confirm the major role that bulk viscoelastic properties play in pressure sensitive adhesive performance, and indicate the power of two methods for direct measures of important properties. We also observed that dynamic mechanical properties some 100°C above the use temperature correlate better with performance than those taken at room temperature, and suggest the discrepancy in strain amplitude as the cause for the apparent shift. Some support for this rationale is found in the observation that correlations of similar quality are obtained using high-strain room temperature properties, (tensile strength and elongation) when available, or small-strain high temperature properties. Use of directly-measured tensile strength has helped to clarify the role of mechanical properties in the mode and energy of the peel process, and similar inferences can be drawn using the high-temperature modulus and dissipation. It is seen that the balance of performance in successful pressure sensitive acrylic adhesives requires materials that simultaneously possess both solid-like strength and liquid-like flow behavior, and that the wide range of peel and shear properties available for specific applications is reflected in a corresponding range of tensile strength, storage modulus, and dissipation shown by the bulk mechanical properties.

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References

1. D. H. Kaelble, *Physical Chemistry of Adhesion* (Wiley, New York, 1971), esp. pp. 423.
2. D. Satas, *Handbook of Pressure Sensitive Adhesive Technology*, 2nd ed. (Van Nostrand Reinhold, New York, 1989), esp. pp. 61, 97, 396.
3. F. H. Wetzel, *ASTM Bull.* **221**, 64 (1957).
4. W. C. Dale, J. K. Haynes, M. D. Paster and E. F. Alstede, Proceedings 1987, Pressure Sensitive Tape Council, Itasca, IL, p. 126.
5. J. C. Richmond, R. E. Wetton and G. M. Foster, Proceedings 1987, Pressure Sensitive Tape Council, Itasca, IL, p. 16.
6. G. Kraus, K. W. Rollman and R. A. Gray, *J. Adhesion* **10**, 221 (1979).
7. Lecon Woo, *Anal. Calorim.* **5**, 155 (1984).
8. T. G. Wood, *Adhesives Age* **30**, 19 (1987).
9. D. Satas, *Adhesives Age* **31**, 28 (1988).
10. S. W. Medina and F. V. DiStefano, *Adhesives Age* **32**, 18 (1989).
11. L. E. Nielsen, *Mechanical Properties of Polymers* (Reinhold, New York, 1962).
12. J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd. ed. (Wiley, New York, 1980).
13. H. H. Winter and F. Chambon, *J. Rheol.* **30**, 367 (1986).
14. C. A. Dahlquist, Proceedings 1988, Pressure Sensitive Tape Council, Itasca, IL, p. 18.
15. E. H. Andrews, *J. Polymer Sci. Symposium No. 72*, 295 (1985).
16. E. H. Andrews and A. J. Kinloch, *J. Polymer Sci. Symposium No. 46*, 1 (1974).
17. H. Eyring, *J. Chem. Phys.* **4**, 283 (1936).
18. G. E. Warnaka, *Rubber Chem. Technol.* **36**, 407 (1963).
19. R. E. Robertson, *Appl. Polymer Symp.* **7**, 201 (1968).
20. R. P. Kambour and R. E. Robertson, in *Polymer Science*, A. D. Jenkins, Ed. (North Holland, Amsterdam, 1972), p. 687.
21. A. S. Argon, *Phil. Mag.* **28**, 839 (1973).
22. C. A. Dahlquist, in *Treatise on Adhesion and Adhesives*, R. L. Patrick, Ed. (Marcel Dekker, New York, 1969), p. 219.
23. W. Druschke, *Adhäsion*, **May 1987**, p. 29. *ibid*, **June 1987**, p. 26. English summary in Ref. 2, pp. 406.
24. A. N. Gent and G. R. Hamed, in *Encyclopedia of Polymer Science and Engineering*, 2nd ed., H. F. Mark *et al.*, Eds. (Wiley, New York, 1985), p. 500.
25. D. H. Kaelble, *J. Adhesion* **1**, 102 (1969).
26. R. J. Good and F. Shoraka, *Amer. Chem. Soc. Symposium 287*, 39 (1985).
27. R. J. Good and R. K. Gupta, *J. Adhesion* **26**, 13 (1988).
28. F. D. Petke in *Adhesion Science and Technology* L. H. Lee, Ed. (Plenum, New York, 1975), p. 177.

APPENDIX

The first reason for using DMA results at high temperature to correlate with room temperature PSA performance was empirical; the high temperature DMA data showed the greatest differences between curves and best correlations with performance. Also, high-strain room temperature tensile test results showed equally good correlations when available. The earliest DMA experiments had used the smallest available strain amplitude, and shown an actual maximum near

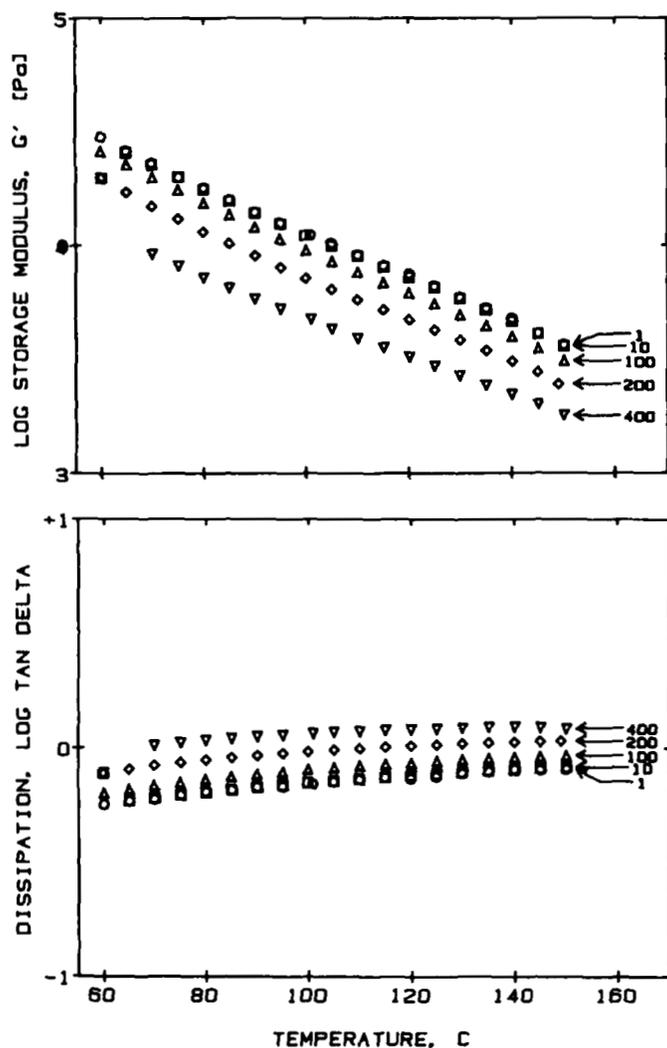


FIGURE A1 Effect of shear strain amplitude on dynamic mechanical properties of a typical GME. Key denotes amplitude in percent.

100°C when r^2 was calculated using room-temperature performance properties and DMA data taken at various temperatures. The results reported here used a larger strain ("×4" on the DMTA) for better signal-to-noise, and the correlations are essentially independent of the specific high temperature chosen. We also occasionally observed additional weaker features in the high-temperature DMA properties of some other acrylic PSA's, not discussed in this paper. Clearly, the specific high temperature chosen must be well removed from such features when they are present.

However, the use of a similarity between high strain and high temperature is not unprecedented. The existence of some kind of reciprocal relation between strain energy and thermal energy dates from at least the Eyring equation for stress-activated flow.¹⁷ For (structural) rubbers, Warnaka¹⁸ has described in detail the nonlinear DMA effects of strains up to 100%, including reduction of G' by as much as one decade, and a corresponding increase in dissipation. For glassy polymers, Robertson,¹⁹ Kambour,²⁰ and Argon²¹ have presented various models for stress-activated flow, the first based on a concept of stress-induced "effective temperature," and the last utilizing a cavitation process which very likely applies as well to "leg" formation in PSA's as to glassy polymers.

In a preliminary experiment to assess strain effects in the present PSA's, one of the GME adhesives was run in a Rheometrics Mechanical Spectrometer at strains up to 400%. The results, in Figure A1, not only confirmed the expected decrease in G' and increase in $\tan \delta$ above the linear limit, but indicated that the modulus shift at 400% strain was equivalent to a temperature increase of about 40°C. The data give qualitative support to use of the modulus at a higher temperature, and indicate that 100°C above use temperature is a plausible choice.