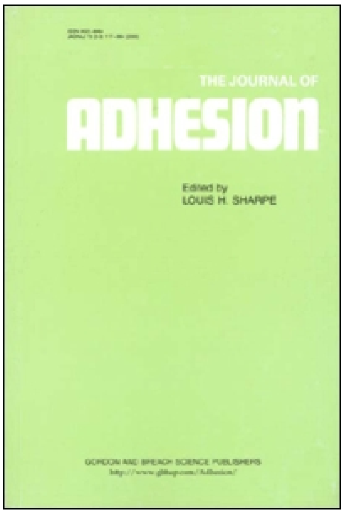

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

New Developments in Structural Adhesives for the Automotive Industry

U. T. Kreibich[a]; A. F. Marcantonio[b]
[a] CIBA-GEIGY AG, Subdivision Plastics, Basel, Switzerland [b] CIBA-GEIGY Formulated Systems Group (Automotive Center), Madison Heights, MI, U.S.A.

To cite this Article Kreibich, U. T. and Marcantonio, A. F.(1987) 'New Developments in Structural Adhesives for the Automotive Industry', The Journal of Adhesion, 22: 2, 153 — 165
To link to this Article: DOI: 10.1080/00218468708074998
URL: http://dx.doi.org/10.1080/00218468708074998

J. Adhesion, 1987, Vol. 22, pp. 153–165
Photocopying permitted by license only

Printed in the United Kingdom

New Developments in Structural Adhesives for the Automotive Industry†

U. T. KREIBICH

CIBA-GEIGY AG, Subdivision Plastics, CH-4002, Basel, Switzerland

A. F. MARCANTONIO

CIBA-GEIGY Formulated Systems Group (Automotive Center), Madison Heights, MI 48071, U.S.A.

(Received October 24, 1986)

Recently developed epoxy paste adhesives, reactive hot melts, adhesive film tape and polyurethane adhesives are presented for structural bonding in the automotive industry. Paste adhesives usually require a precure stage to obtain handling strength of the joints and to guarantee wash-out resistance of the adhesive in the paint baths. This step can be omitted with reactive hot melts and adhesive film tape, which are solid before and after their application. In addition they allow an improved working hygiene. Some mechanical properties of the adhesives are shown such as lap shear strength and peel strength as well as lap shear strength as a function of the bondline thickness. Results of the excellent durability of epoxy one-component pastes, reactive hot melts and adhesive film tape are given from cyclic environmental and salt spray tests.

KEY WORDS Epoxy adhesives; polyurethane adhesives; reactive hot melts; adhesive film tape; mechanical properties; environmental resistance.

1 INTRODUCTION

During recent years adhesive joints have received increasing interest in the automotive industry with emphasis

- to reduce and even eliminate spotwelding of steel,

† Presented at the Tenth Annual Meeting of The Adhesion Society, Inc., Williamsburg, Virginia, U.S.A., February 22–27, 1987.

- to improve corrosion resistance,
- to bond substrates, especially polymers, which cannot be joined by conventional fastening techniques,
- to allow engineers new ways in the construction of vehicles and to reduce the number of parts of a car,
- to improve the efficiency of production lines.

Similar to adhesives for the aircraft industry, structural adhesives used by the automotive industry have to fulfill demanding performance profiles with respect to the mechanical and environmental properties of the joint, the application and curing properties of the system as well as to its storage conditions (see Figure 1). Critical for good adhesion are defined chemical and physical properties of the substrate surface and its interactions with the adhesive.[1–3] In contrast to the well-defined surfaces of the aircraft industry, *e.g.* pretreated aluminium,[4,5] car manufacturers extensively use oily steel and are reluctant to invest in surface pretreatment because of the incurred cost premium.

Major developments are ongoing to fulfill the requirements for engineering adhesives. Out of these only a few highlights can be given now on epoxy paste adhesives, reactive hot melts, adhesive film tape and two-part polyurethane adhesives.

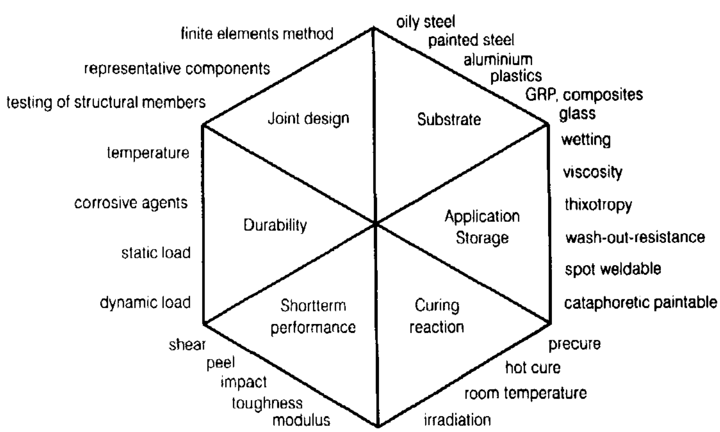

FIGURE 1 Major factors determining performance of an adhesive for the automotive industry.

Some typical and important aspects of their application and curing characteristics, their mechanical strength and their environmental durability will be dealt with.

2 APPLICATION AND CURING PROPERTIES

When epoxy or polyurethane adhesives crosslink in a polyaddition reaction, a polymer is formed with a glass transition, T_g, varying with the structure.[6] The T_g shifts to higher temperatures as the degree of reaction and the crosslinking density increases.[7] Figure 2 shows the typical scanning calorimetric profile of the reaction of the epoxy resin bisphenol-A diglycidylether with the hardener diaminodiphenylmethane, at different stages of cure. Towards increasing temperatures T_g is followed by an exothermic peak, until complete cure has been accomplished. The area of the peak is calculated to give the reaction enthalpy and the degree of cure. The higher the degree of cure, the better normally becomes the mechanical and environmental performance.[8]

Figure 3 shows the typical curing reaction of bisphenol-A

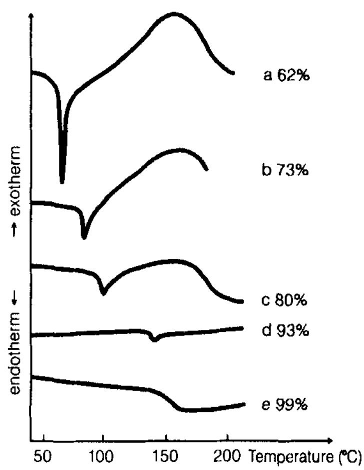

FIGURE 2 Glass transition, T_g, and exothermic reaction of an epoxide system as a function of the degree of reaction (DSC-diagram, heating rate = 10°/min). Epoxide system: Bisphenol-A diglycidylether + diaminodiphenylmethane.

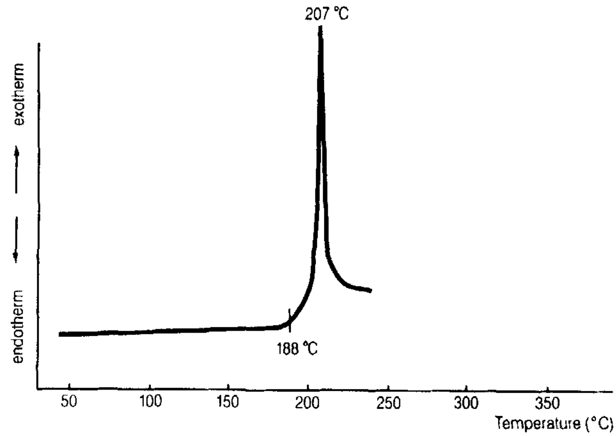

FIGURE 3 Curing reaction of bisphenol-A diglycidyl ether with dicyandiamide (DSC-diagram, heating rate = 20°C/min).

diglycidyl ether with dicyandiamide in air atmosphere. When the exotherm is measured as a function of time, in the isothermal mode, the extent of cure can also be calculated. Small amounts of accelerators or catalysts can be seen to shift the exotherm to lower temperatures, as seen in Figure 4.

Another important property, the rheological behaviour of a

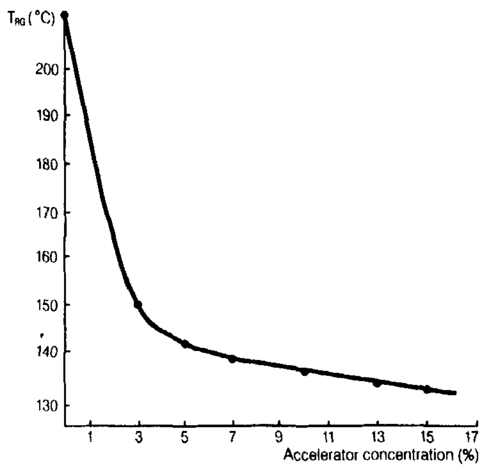

FIGURE 4 Temperature T_{RG} of the exothermic reaction maximum of an epoxy system as a function of the amount of accelerator (experimental product).

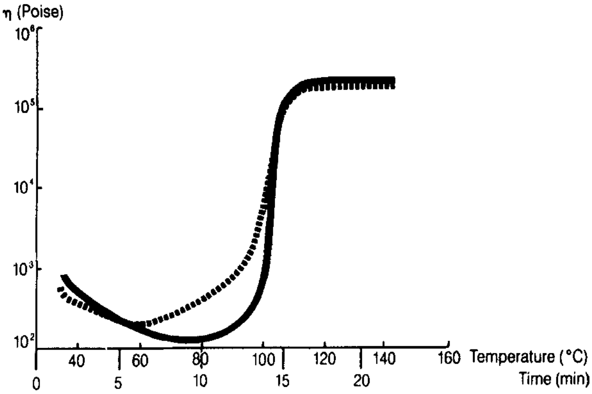

FIGURE 5 Dynamic flow viscosity of epoxy-2-part adhesives as a function of temperature and time. — XW 455-A2 and - - - LSU 202-41, both cured with XW 441-B2.

typical thermoset adhesive, is shown in Figure 5. The dynamic flow viscosity of the epoxy resin is automatically plotted with time and temperature (Rheometrics RDA-700 Dynamic Analyzer). The viscosity of the adhesive can be obtained at any temperature or time at a specific heating rate before gelation occurs.[9] A graph of the viscosity at constant temperature with time measures the stability of the adhesive (see Figure 6).

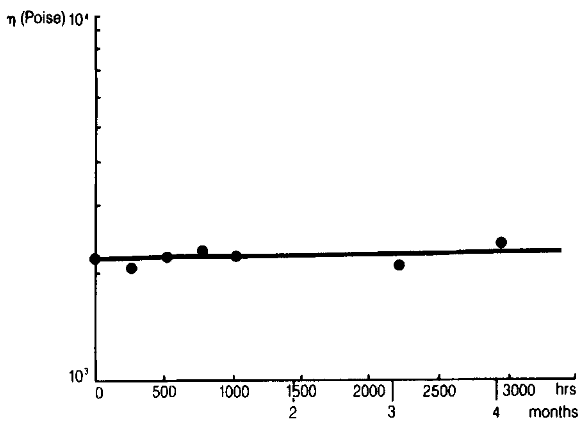

FIGURE 6 Stability of an epoxy-1-part adhesive, RW 213-37, at 75°C as a function of its storage time at RT from measurements of the dynamic flow viscosity.

The basic relationship between the chemical structure of the components of a system, the curing reaction and the material properties have to be used in order to fulfill the demanding performance profiles of adhesives for the automotive industry. Usually, the best performance can be achieved with heat curing systems. In the car industry the heat of the paint baking process is used to effect this cure. However, for the handling of parts on a production line an initial or green strength is needed for an adhesive joint prior to passing through the ovens for paint baking. In addition, the solidification prevents paste adhesives from contaminating cataphoretic paint baths. Depending on the chemical structure of the reaction partners, adhesives can be formulated with a tailor-made precure time to achieve handling strength (see Figure 7). This green strength is already obtained for new one-component epoxy paste adhesives after a few seconds of induction precure or some minutes of oven precure. These minimum reaction times at certain bondline temperatures can be increased, if required for application.

With two-part epoxy adhesives handling strength at room temperature is obtained after a reaction time of 10–20 min, which decreases with higher temperatures. The low heat conductivity of parts made from fibre-reinforced polyester, *e.g.* sheet molding compound (SMC), bulk molding compound (BMC) etc., increases

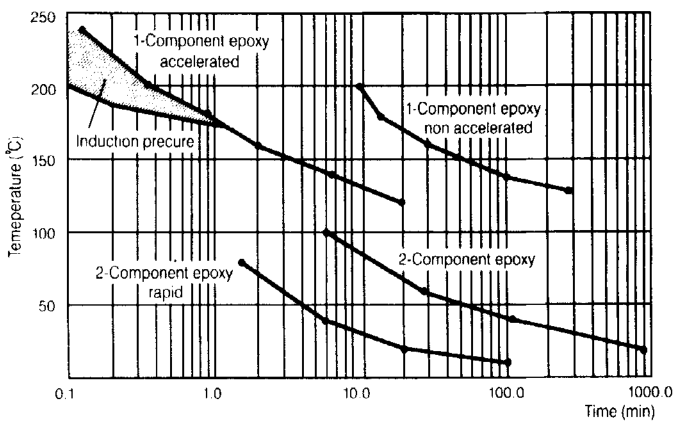

FIGURE 7 Time until handling strength at different temperatures for various 1- and 2-part epoxy adhesives.

the time required for the curing cycle. Therefore, more reactive adhesives are needed. So two-part epoxy adhesives have been formulated with cycle times for manufacturing of even 1.5 min at 80°C at a pot life of about 4 min.

Another important factor for adhesive application is its physical form, which is again dependent upon the chemical formulation. Although car manufacturers are more and more using application robots on production lines, working hygiene gains increasing interest. New adhesives have been developed which are applied in the solid state as adhesive film tape and interest is now being expressed in adhesives which are solidified during application as reactive hot melts. Such adhesives are wash-out resistant and save the precuring step.

3 MECHANICAL PROPERTIES

With the application of adhesive to bond primary structures, impact resistance is of some concern to the automotive makers. Epoxy adhesives are thermally durable, but can be quite brittle unless modified for impact resistance.[10–13] Both the chemistry of modifying adhesive epoxy systems for impact resistance, while allowing little or no sacrifice to processing, mechanical properties, and environmental resistance, and methods development for toughness evaluation, are currently the subjects of intensive research efforts. A great deal of attention has been focused on the toughness (impact resistance) of thermoset matrix resins used in composite technology.[14,15] Similar methods can be applied to the toughness of adhesives.

Typical examples of the lap shear strength, the T-peel, and the roller peel of one-component pastes, of reactive hot melts, and of adhesive film tape are presented in Figure 8 to illustrate the possibilities of formulation and flexibilization. The T-peel of one-component paste adhesives, a critical property in engineering, can be significantly improved by formulation as seen from the comparison of pastes 1 and 2. New reactive hot melts are under development. They can be formulated to have properties varying from those of high strength adhesives to sealant type products. With film adhesives the possibilities of formulation to change properties is

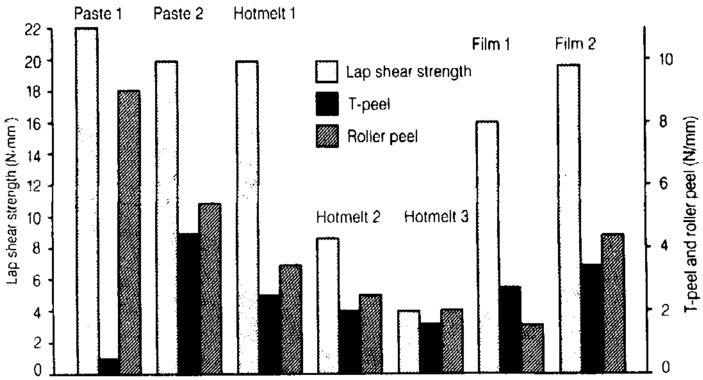

FIGURE 8 Lap shear strength, T-peel and roller peel of epoxy-based 1-part paste adhesives, reactive hot melts and adhesive film tape. Cure: 30 min at 180°C, Substrate: Steel, oiled.

more restricted. So the key to a high performance adhesive, fulfilling the demanding specifications of the automotive industry, is the creative choice and careful balance of the ten or more compounds making up an adhesive, many of which can react or interact with each other. Of course, the adhesive strength depends on its relaxation behaviour with temperature. A significant change is observed during the glass transition.

The strength of an adhesive joint strongly depends on the stresses imposed during the tests. Especially the most common test methods such as the lap shear test and the peel test show rather inhomogeneous stress distributions depending on the geometry of the test specimen and the stress environment.[16] Adhesive strength is also influenced significantly by the bondline thickness. Joints of aluminium and SMC with epoxy adhesives show a decay of the lap shear strength with increasing bondline thickness (see Figure 9). The effect is the more pronounced, the higher the resistance of the adhesive and of the substrate is to deformation.

In Figure 9 the reactive hot melt shows cohesive failure in the bondline of the aluminium joints, whereas material failure is observed in the SMC, *i.e.* pull-out of glass fibres, with two-part epoxy and polyurethane adhesives at all bondline thicknesses considered. The fact, that SMC fails at different levels of load (see Figure 9) can be explained by the increased resistance of the lap

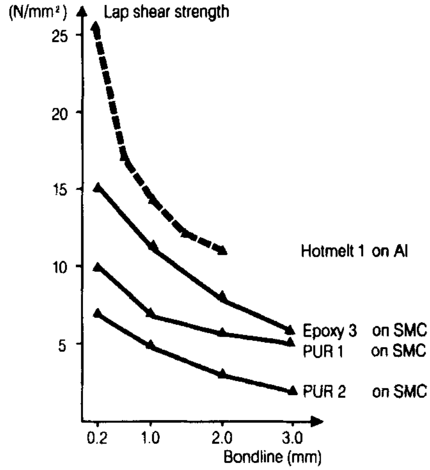

FIGURE 9 Lap shear strength of a reactive hot melt and of epoxy and polyurethane 2-part adhesives as a function of the bondline thickness. Substrates: SMC with E-modulus 10000 N/mm^2, Aluminium, Test: Lap shear strength after ISO 4587.

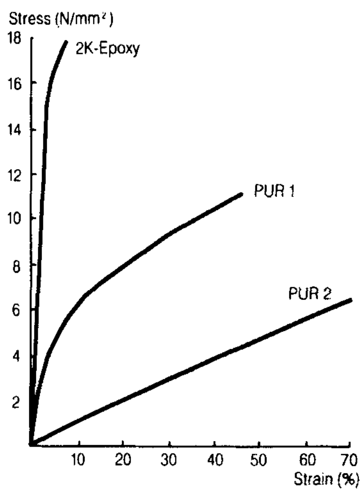

FIGURE 10 Stress-strain-diagrams of epoxide and polyurethane 2-part adhesives. Test: Tensile test after ISO R 527.

shear specimens towards bending moments and plastic deformations under stress depending on the elastic modulus of the adhesives used. Stress-strain diagrams in Figure 10 show the higher elastic modulus of the epoxy adhesive compared with the polyurethane adhesives with higher energy absorption and higher elongation.

This comparison of data illustrates the importance of stress analysis which affects the components as shear stresses, normal stresses and their superpositions. The choice of the test method and the test geometry is crucial, in order to obtain relevant results from calculations for design with adhesives. Suitable data are provided, *e.g.*, by measurements of tubular, blunt-joined test specimens in the tensile-torsion test.[17]

4 ENVIRONMENTAL DURABILITY

Adhesives for the automotive industry have to match with the lifetime of a car without major changes in strength and aspects of failure. The durability of adhesive joints in corrosive environments heavily depends on the chemical interlocking of the adhesive and

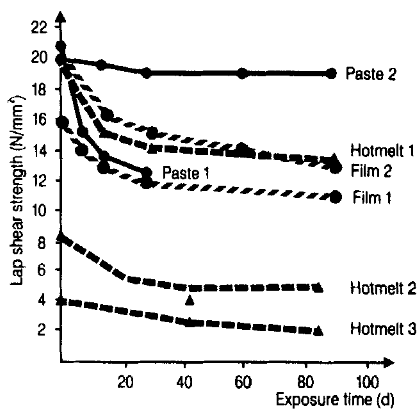

FIGURE 11 Cyclic environmental resistance of epoxy-based 1-part adhesives, reactive hot melts and adhesive film tape as a function of the exposure time (cycles: −20°C to + 70°C/100% rel. humidity). Cure: 30 min at 180°C, Substrate: Steel, oiled, Test: Lap shear strength after ISO 4587.

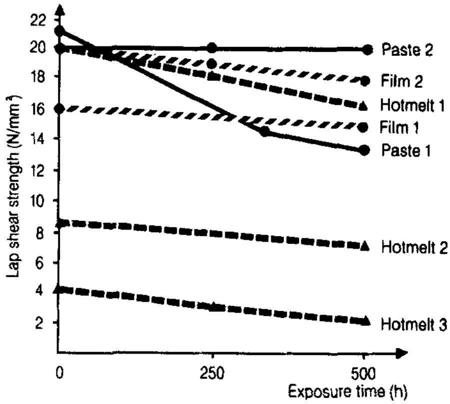

FIGURE 12 Saltspray resistance of epoxy-based 1-part adhesives, reactive hot melts and adhesive film tape in function of the exposure time. Cure: 30 min at 180°C, Substrate: Steel, oiled, Test: Lap shear strength after ISO 4587.

the substrate surface. Cyclic environmental and salt spray test are well established methods to predict the durability of adhesive joints from accelerated aging. They combine the effect of plastification and the chemical effect of degradation of the adhesive joint by water or salt solutions, which reduce the adhesive strength. The evidence of these tests is, however, limited, especially if they are performed at elevated temperatures. Then the polymer can be in the rubbery state. This facilitates the penetration of humidity and solutions into the polymer network over that in the glassy state, which is the typical physical state of many structural adhesives in the joint.

Figure 11 shows the excellent corrosion resistance of adhesive joints of oily steel with the epoxide paste adhesive 2, the reactive hot melt 1 and the adhesive film types for 90 days exposure. But, also, the semistructural and the sealant type reactive hot melts 2 and 3 show improved durability, always at cohesive fracture of the adhesive. This is especially remarkable, since the flexible, rubbery phase dominates in highly flexible adhesives.

Salt spray tests after DIN 50 021 with lap shear samples (see Figure 12) also show an outstanding durability of the new paste generation 2, the reactive hot melts and the adhesive film tape.

5 CONCLUSION

New generation paste adhesives are under development. They show handling strengths after short induction cure, improved toughness and environmental resistance. Excellent mechanical properties and durability can also be achieved with new solid adhesives. They are applied as reactive hot melts with different degrees in flexibility or as adhesive film tape. Comparisons of strength data obtained with different test methods show the big influence of geometry of the specimens, the stresses applied and the bondline thickness. In addition, the modulus and the behavior in plastic deformation of both substrate and adhesive are determining factors. This needs proper consideration and the design of adhesive joints for optimum strength now becomes a crucial factor for the usage of adhesives in the automotive industry.

Acknowledgement

The authors would like to thank H. Lehmann, Dr. K. Mechera, Dr. H. Simon, K. Urech, Dr. J. Weber and J. Hack for their valuable contributions.

Designations of Experimental Products (all are from Ciba-Geigy)

EP-Paste 1	= XD 911
EP-Paste 2	= Le 10193.6
EP-Hotmelt 1	= JW 873.6
EP-Hotmelt 2	= JW 974.2
EP-Hotmelt 3	= JW 973.1
EP-Film 1	= KU 868
EP-Film 2	= KU 920
Epoxy 3	= Le 10192 + Le 10168 (1:1)
PUR 1	= HS 1212 + HS 1308 (1:1)
PUR 2	= HS 1026 + HS 1116 (1:1)

References

1. D. H. Kaelble, *Physical Chemistry of Adhesion* (Wiley Interscience, New York, 1971).
2. W. A. Zisman, in *Handbook of Adhesives,* I. Skeist, Ed. (Van Nostrand Reinhold, New York, 1977).
3. L.-H. Lee, *Adhesive Chemistry, Developments and Trends* (Plenum Press, New York and London, 1984).

4. W. Brockmann, O. D. Hennemann, H. Kollek, and C. Matz, *Adhaesion* **7/8,** 31 (1986).
5. W. D. Saunders, *Adhesives Age,* August, 1986, p. 39.
6. U. T. Kreibich and H. Batzer, *Angew. Makromol. Chem.* **83,** 57 (1979).
7. H. Batzer, F. Lohse, and R. Schmid, *Angew. Makromol. Chem.* **29/30,** 349 (1973).
8. T. Daniels, *Thermal Analysis* (John Wiley and Sons, New York, 1973).
9. C. W. Macosko, *Adhesives Age* **20,** 35 (1977).
10. E. Forster, in H. Batzer, *Polymere Werkstoffe, Band III, Technologie 2* (Georg Thieme Verlag, Stuttgart, New York, 1984).
11. U. T. Kreibich, E. Lohse, R. Schmid, and G. Wegner, Einfluss Struktureller Merkmale, in H. Batzer, *Polymere Werkstoffe, Band I, Chemie und Physik* (Georg Thieme Verlag, Stuttgart, New York, 1985).
12. A. J. Kinloch, in K. Dusek, *Epoxy Resins and Composites I* (Springer-Verlag Berlin, Heidelberg, New York, Tokyo, 1985).
13. A. F. Yee and R. A. Pearson, *J. Mater. Sci.* **21,** 2462 (1968) and 2472 (1986).
14. "Standard Tests for Toughened Resin Composites", NASA Reference Publication 1092 (1983).
15. J. Harper-Tervet, *27th National SAMPE Symposium* **27,** 292 (1982).
16. R. D. Adams and W. C. Wake, *Structural Adhesive Joints in Engineering* (Elsevier Applied Science Publ., London, New York, 1984).
17. J. Engasser and A. Puck, *Kunststoffe* **70,** 423 (1980).