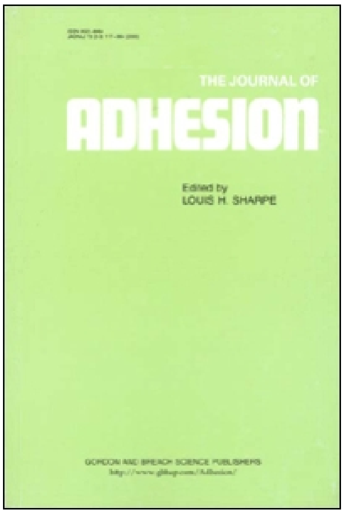

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Semi-Structural Hot Melt Adhesives Based on Crosslinkable Functionalized Polyolefins*

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A structural or semi-structural adhesive is usually applied to the substrates as monomers, oligomers, or melts of polymers with reactive groups and is then polymerized or crosslinked *in situ* in the joint between the substrates. We have been studying a number of crosslinked functionalized polyolefins blended with tackifier used as semi-structural adhesives for bonding to oily galvanized steel surfaces. The functions of takifier, surface properties of adhesive and substrate, geometry effects of lap joints, adhesive T_β, chain end defects, network chain length, and cure kinetics of these systems will be discussed. Our experimental results indicate that lap shear strengths of galvanized steel joints depend on adhesive storage modulus to the power of roughly 1/2. A rough estimate of the fracture energy of the adhesive bond, G_a, could be obtained from this relation. Although some estimated G_a values are too low while the others are too high, they seem to be in rough accord with the degree of interfacial bonding and the locus of failure of the lap shear bonds.

KEY WORDS: Hot melt adhesive; functionalized polyolefin; tackifier; automotive industry; lap shear; galvanized steel; crosslink; fracture energy; storage modulus.

INTRODUCTION

A structural or semi-structural adhesive is usually applied to the substrate as monomers, oligomers, or melts of polymers with reactive groups. It is then polymerized or crosslinked *in situ* in the joint between the substrates (Fig. 1). We have been studying several functionalized polyolefins blended with tackifier, and epoxy, or epoxy/acid anhydride. These blends are applied as a hot melt to oily galvanized steel substrates and subsequently crosslinked by heat curing. The functionalized polyolefins used include ethylene/acrylic acid copolymers (EAAs), ethylene/methyl acrylate/acrylic acid terpolymers (EMAAAs), partially hydrolyzed EVAs (ethylene/vinyl acetate/vinyl alcohol terpolymers; EVAVOHs), and ethylene/2-hydroxyethyl methacrylate copolymers (EHEMAs) shown in Fig. 2. These crosslinked polyolefin adhesives have enhanced high temperature properties. In addition, no low molecular weight by-products are generated in the condensation reaction between the

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- **Definition**
  - **Bond Polymerized/Crosslinked In situ Between Rigid Substrates.**
  - **High Shear/Peel Strength In Hostile Environments.**
  - **Non-Interfacial Failure (Adhesive Must Fail Cohesively Or Substrate Must Fail.)**
- **Typical Formulations**
  - ***Conventional***

Component	**Role**	**Concentration (phr)**
Resin (Epoxy)	**Polymer Backbone**	**100**
Hardener (Amine)	**Crosslinking Agent**	**0-10**
Reactive Rubber	**Toughening Agent**	**0-20**

- ***Some Exxon Approaches***

Component	**Role**	**Concentration (phr)**
Functionalized Polyolefin	**Polymer Backbone/Toughening**	**100**
Hardener (Epoxy/Anhydride)	**Crosslinking Agent**	**10-50**
Tackifier	**Cured System Tg Control;** **Hot Melt Viscosity Control**	**100-200**

FIGURE 1 Structural and semi-structural adhesives.

acid and the epoxy groups. Therefore, the adhesive/substrate interface is free of impurities. Also, failure of these adhesive joints is generally cohesive. These properties fulfill the strength requirements of semi-structural adhesives used in the automotive industry. The functions of tackifier, surface properties of adhesive and substrate, joint geometry effects, adhesive T_β, chain end defects, and network chain length of these systems will be discussed.

EXPERIMENTAL

Table I shows the characteristics of these functionalized polyolefins. Melt index (MI) was measured according to ASTM D1238, condition E, 190°C and 2.16 kg. Number

TABLE I
Characterization of Functionalized Polyolefins

Polymer	MI	M_n	Wt. %		T_β°C	T_m,°C
EMAAA 1	16	--	MA = 20	AA = 7	−34	65
EMAAA 2	160	--	MA = 10	AA = 8	−32	82
EMAAA 3	260	--	MA = 22	AA = 1	−36	75
EMAAA 4	345	--	MA = 18	AA = 11	−25	60
EAA 1	40	--	--	AA = 15	−30	90
EAA 2	300	--	--	AA = 20	25	80
EAA 3	1790	--	--	AA = 12		
EVAVOH 1	--	5800	VA = 4.0	VOH = 13.7	−22	91
EVAVOH 2	--	7500	VA = 11.3	VOH = 9.25	−20	81
EHEMA	--	1000	--	HEMA = 35.8	−32	76

MA = Methyl Acrylate, AA = Acrylic Acid, VA = Vinyl Acetate,
VOH = Vinyl Alcohol, HEMA = 2 – Hydroxyethyl Methacrylate

average molecular weight (M_n) was determined by GPC. T_β and T_m of each polymer were measured by DSC. Tackifiers used include Escorez 1310LC[1], an aliphatic-aromatic tackifier, and a rosin ester tackifier. As shown in Fig. 2, the diglycidyl ether of bisphenol-A was the diepoxy crosslinking agent, and pyromellitic dianhydride (PMDA) was the acid anhydride used. In some formulations, phthalic anhydride (PAH) was also used. Galvanized steel coupons (10.2cm × 2.5cm × 0.15cm (4″ × 1″ × 0.06″); sheet galvanized ASTM A525 G-90) were degreased and then greased by the following method. After being immersed in acetone and wiped clean by lint-free paper, they were dipped into a heptane solution of ASTM oil #3 (heptane/oil volume ratio = 9/1). Each coupon was then hung and dried in the fume hood for about 30-90 minutes. It was estimated that there was about 3 g/m^2 of oil deposited on the galvanized steel surface after this treatment.

Each adhesive blend was prepared by hot melt mixing. After solidification, the uncured solid adhesive blend was pressed at 100°C for 5-10 s to form a sheet with a thickness of 254-305 µm (10–12 mils) upon cooling. The sheet was then cut into 2.54 × 1.27 cm (1″ × 1/2″) slabs. One of them was clamped between two oily galvanized steel rectangular coupons using 0.02 cm (8 mils) wires as spacers. The clamped coupons were cured in an oven at 180°C for 30 minutes. Lap shear tests were conducted according to ASTM D-1002-72.

Cure kinetics of adhesives was studied by using a Monsanto Oscillatory Rheometer at 140°, 160°, 180° and 200°C. If Γ is the rotor torque at time t, the reaction rate, R', of crosslinking is defined as: $R'(t) = [\Gamma_{\max} - \Gamma(t)]/[\Gamma_{\max} - \Gamma_{\min}]$.

Two environmental performance tests were used. In the simulated salt spray test, lap shear strength of the galvanized steel joint at room temperature after attack in a 5% NaCl bath at 35°C for a 1–3 week immersion period was measured. In the "wet cataplasm" test, the joint was aged at 70°C/100% relative humidity for a 1–3 week

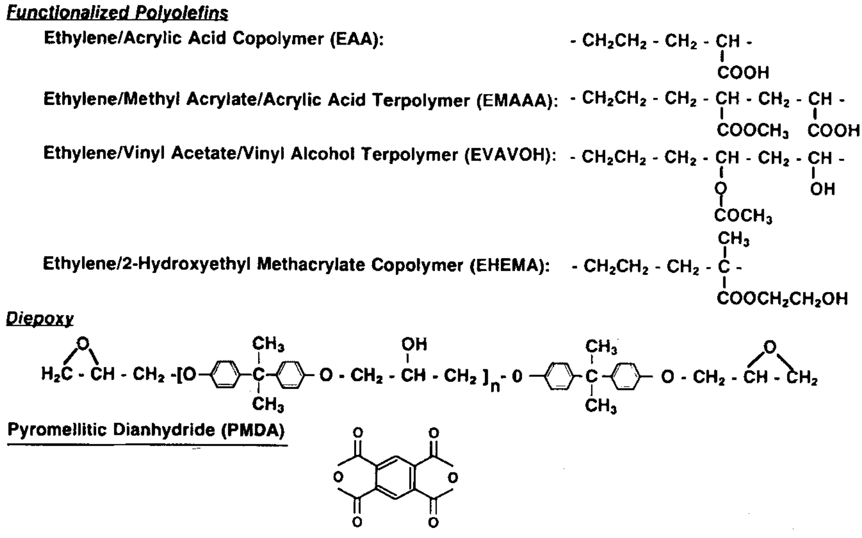


FIGURE 2 Functionalized polyolefins and crosslinking agents.

period. After 1, 2 or 3 weeks, the joint was held at $-10°C$ for 2 hours. Lap shear testing at room temperature was performed after the sample was conditioned for 3 hours under ambient conditions.

Experimental details of viscoelastic and contact angle measurements have been described elsewhere.[1,2] A Rheometrics System IV rheometer with torsion rectangle fixture was employed for the viscoelastic experiments. Temperature scan dynamic mechanical measurements were carried out at a frequency ω in accordance with the lap shear debonding frequency (~ 5 rad/s) calculated as shown by the following equation:

$$\omega = 2\pi v/h_a$$

where v is the Instron crosshead speed and h_a is the adhesive thickness.

RESULTS AND DISCUSSION

Functions of Tackifier

Tackifier in the crosslinkable polyolefin adhesive reduces cost and melt viscosity of the adhesive. More importantly, it acts as a hot melt solvent to reduce "screening" between functional groups of the polymer and the crosslinking agent. In a compatible tackifier environment, the functionalized polyolefin chains will be extended so that the functional groups are more accessible to crosslinking.

A compatible tackifier usually raises the T_β (or T_g) of the crosslinked network, enhancing rigidity of the adhesive bond. Tackifier also alters adhesive surface characteristics. Fig. 3 shows the contact angles of water for the galvanized steel substrate without oil treatment, two functionalized polyolefins [EVAVOH 1 and EMAAA 3], and the polymers blended with tackifiers (polymer/tackifier wt. ratio = 2/3), where WBL represents weak boundary layer. The neat polymers have contact angles of water quite close to that of steel. Addition of a compatible tackifier such as rosin ester to EVAVOH 1 could produce an adhesive surface more compatible with steel, as shown by a contact angle even closer to that of steel. On the other hand, addition of Escorez 1310LC could produce a nonpolar adhesive surface, as shown by a higher contact angle of water. This less compatible tackifier may migrate to the interface to form a weak boundary layer, hence weakening interfacial interactions.[2] Therefore, it is not too surprising to observe that, as discussed later, polymer/tackifier compatibility can govern the failure mode of the galvanized steel adhesive joints.

Crosslinking Chemistry

The crosslinking chemistry involving diepoxy and functionalized polyolefins is shown in Fig. 4. For acid–containing polyolefins such as EMAAA, and EAA, if the carboxyls of two different polymeric chains open the epoxy rings of the same epoxy molecule, then the two macromolecules will be joined by a hydroester linkage. On the other hand, hydroxyl-containing polyolefins such as EVAVOH and EHEMA are converted into acid-containing polyolefins by reacting the original polymers with an acid anhydride. The same chemistry described above is then used to crosslink these newly–generated, acid–containing macromolecules by diepoxy molecules.

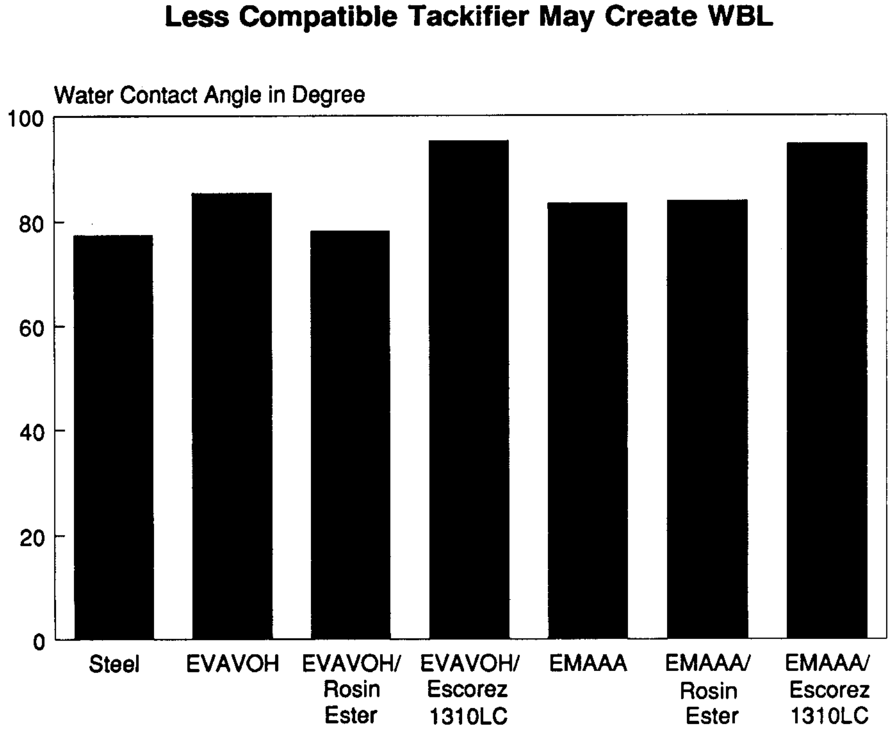


FIGURE 3 Tackifier alters adhesive surface characteristics.

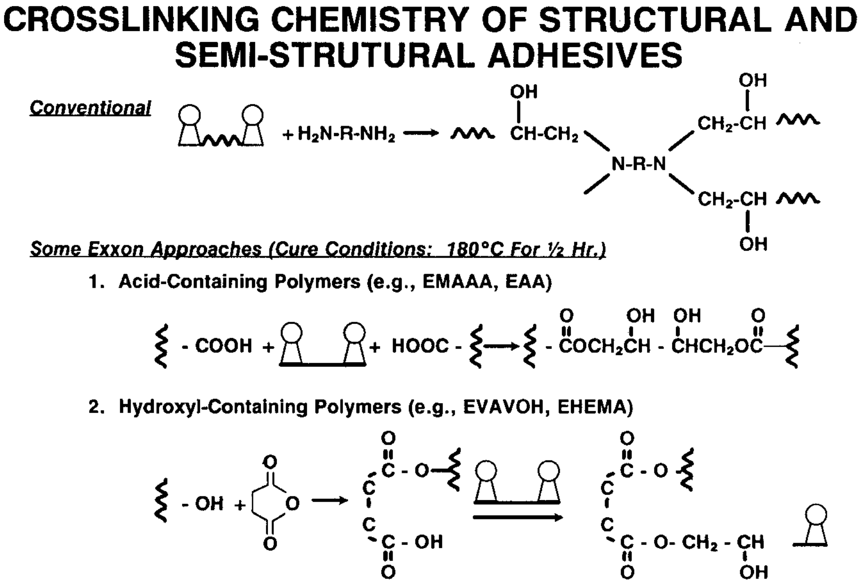


FIGURE 4 A conventional structural adhesive and two new approaches in semi-structural adhesive based on functionalized polyolefin.

Prior to the preparation of the lap shear specimens for each crosslinkable polyolefin adhesive, viscoelastic temperature scan measurements on the cured and uncured adhesives are carried out to confirm the crosslinking reaction. These experiments show the retention of storage modulus of the cured material up to 200°C (see later discussion and Fig. 11). On the other hand, the storage modulus of the uncured material falls sharply near the T_m of the functionalized polyolefin, which is always lower than 100°C (Table I).

Effects of Lap Joint Geometry

The geometry effects (different overlap lengths, l_a's, and bondline thicknesses, h_a's) on failure load have been studied using the formulation: EVAVOH 2/rosin ester/diepoxy/PMDA = 2/3/0.79/0.47 in wt ratio. Fig. 5 shows that failure load (F_f/w), expressed as force per unit width of joint (w), is related to lap shear stress (τ_f) by: $\tau_f = (F_f/w)/l_a$. The relationships of failure load to overlap length and adhesive thickness are shown in Figures 6 and 7. As shown in Fig. 6, failure load appears to increase with increasing overlap length at a given bondline thickness, possibly up to a plateau value. This is a known observation.[3,4] It arises from the maximum shear stress concentrations, τ_c's (Fig. 5, where F is the tensile force applied to the lap joint) in the adhesive layer which occur close to the ends of the overlap. These maximum shear stress concentrations also increase with increasing overlap length. When a certain overlap length is reached, there is no further gain in failure load. For some of the longest overlap lengths, the joint can carry such a high load that tensile fracture of the steel substrate occurs leaving the adhesive bond intact (Fig. 8). For the joints with shorter overlap lengths, the adhesive bond fails cohesively.

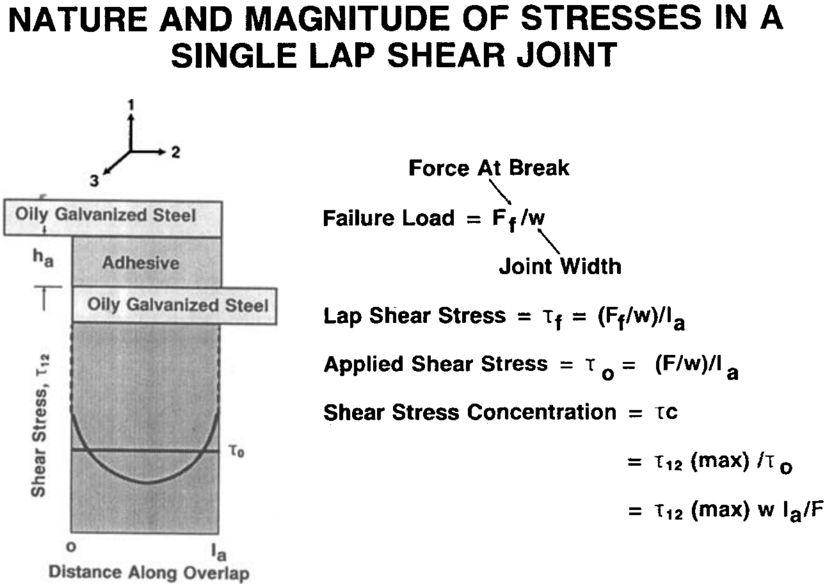


FIGURE 5 Mechanics of a single lap shear joint.

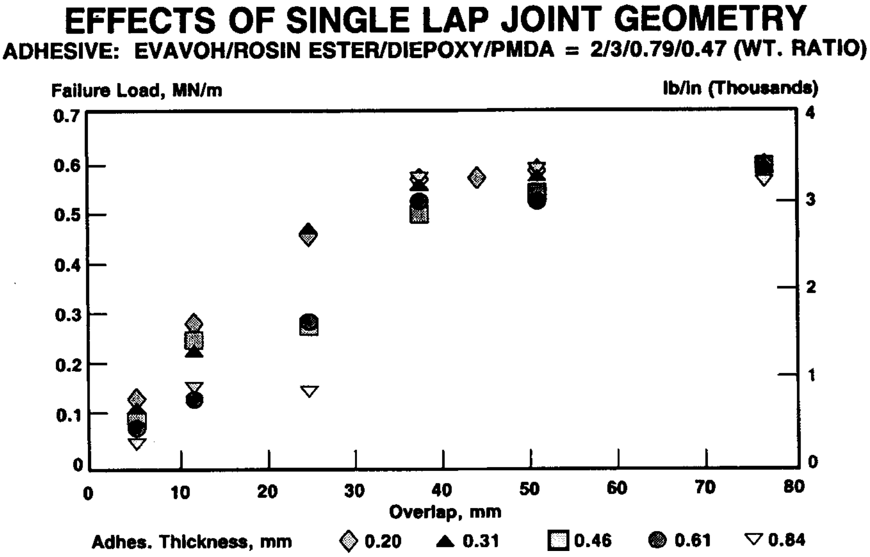


FIGURE 6 Failure load of single lap joints increases and finally reaches a plateau with increasing overlap length.

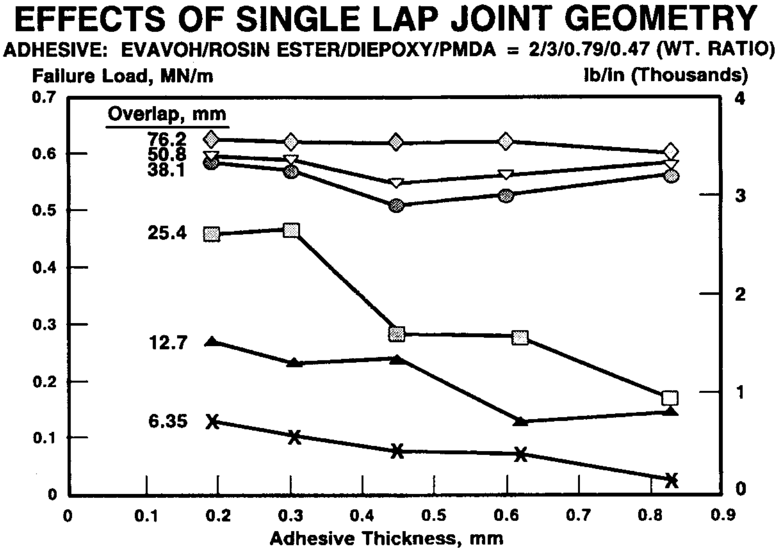


FIGURE 7 Failure load of single lap joints remains constant or drops slightly with increasing adhesive thickness.

Fig. 7 shows that failure load decreases slightly with adhesive thickness for small overlap lengths (6.35 – 25.4 mm) but remains quite constant for large overlap lengths (38.1 – 76.2 mm). Similar behavior has been reported for epoxy/aluminum alloy single lap joints.[5]

AN EXAMPLE OF STEEL SUBSTRATE FAILURE

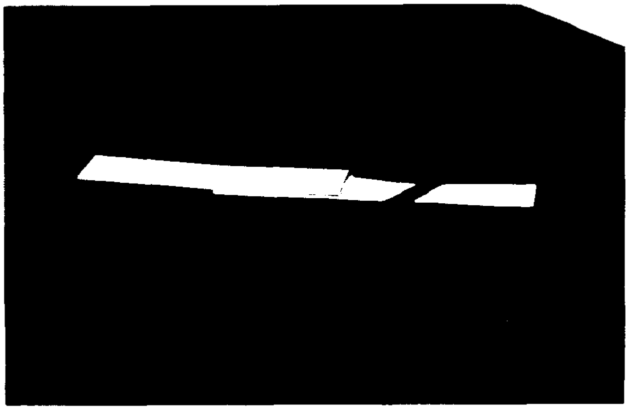


FIGURE 8 At a 50.8 mm (2") overlap length, the steel substrate fails before the fracture of the adhesive bond. See Color Plate.

Fig. 9 shows that the lap shear strength decreases with increasing overlap length at a given bondline thickness. Again, this is directly reflected by the fact that the shear stress concentrations in the joint locate in the vicinity of the ends of the overlap and their magnitudes are proportional to the overlap length. There is more deviation from this behavior for thicker bonds. Lap shear seems to fall with increasing adhesive thickness at the smallest overlap length. As a consequence, at the largest

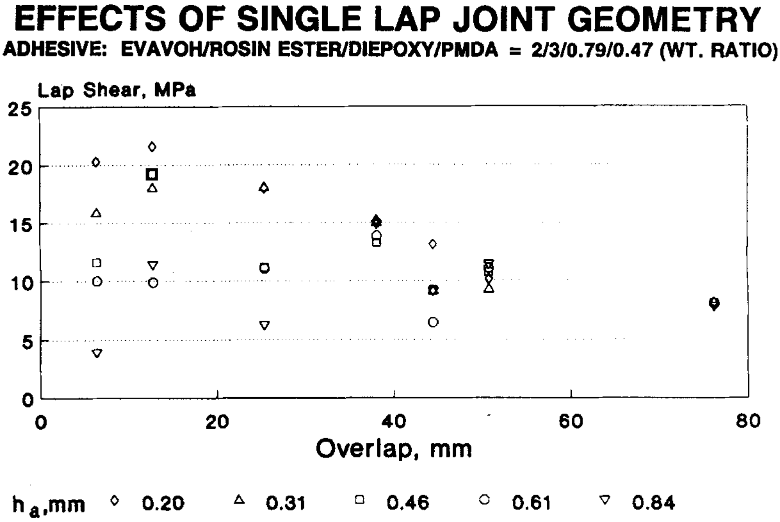


FIGURE 9 The variation of lap strength with overlap length changes with bondline thickness.

thickness studied here, the lap shear actually goes through a maximum at some intermediate overlap length. Again, similar to the behavior of failure load, lap shear strengths at different adhesive thicknesses almost coincide at the same value at the largest overlap.

Effects of Tackifier

Adhesive shear performance and structural parameters depend strongly on the tackifier used in the formulations, as shown by the various epoxy/PMDA crosslinked EVAVOH 2 polymeric systems in Fig. 10. Polymer/tackifier wt. ratio is 2/3. M_c, the average molecular weight between crosslinks in the adhesive network, is determined by the equation: $M_c = \rho RT/G_N$, where ρ is density, R is gas constant, and G_N is the plateau value of storage modulus at an elevated temperature, T (Fig. 11a), or the minimum storage modulus value when the crosslinked adhesive is in its rubbery state (Fig. 11b). Therefore, the formulation containing rosin ester performs better than the formulation containing either Escorez 1310LC or the aliphatic–aromatic tackifier, which, in turn, performs better than the adhesive without any tackifier. According to DSC and viscoelastic temperature scan measurements, in the presence of a compatible tackifier such as rosin ester, the crosslinked adhesive becomes totally amorphous (results not shown here). On the other hand, in the absence of a tackifier or in the presence of a less-compatible tackifier, the crosslinked adhesives still show a certain degree of crystallinity (T_m of EVAVOH = 81 – 91°C). It appears that, for a given base polymer such as EVAVOH 2 at a certain primary molecular weight (molecular weight before crosslinking), the higher T_β adhesives usually exhibit better shear performance. The effects of polymer primary molecular weight or melt index (MI) on adhesive performance will be discussed in the next section.

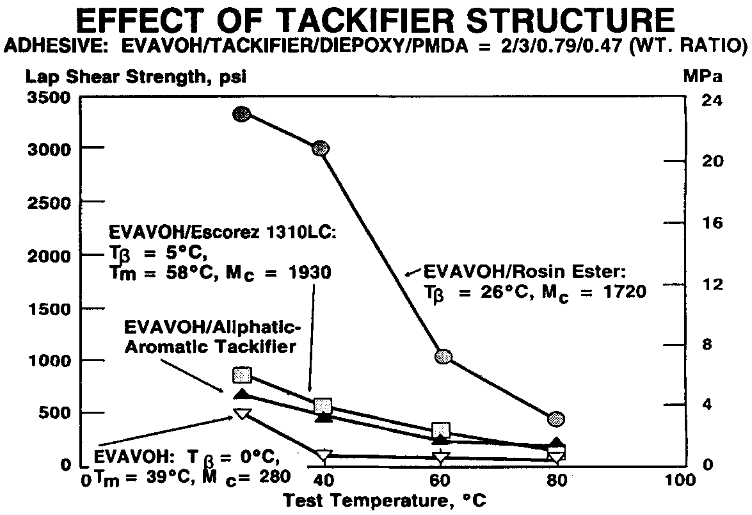
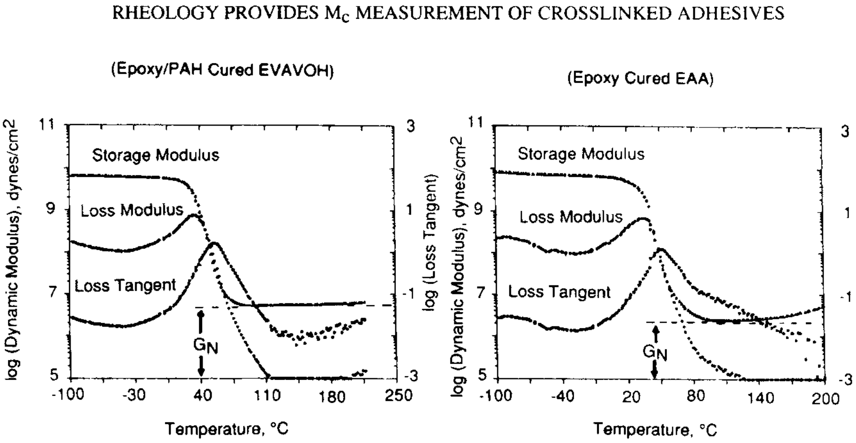


FIGURE 10 Effect of tackifier on lap shear strength of EVAVOH crosslinked by diepoxy/PMDA.



(a) (b)

FIGURE 11 Methods of determining the average molecular weight between crosslinks, M_c, of crosslinked adhesives from Rheometrics temperature scan curves.

Effects of Polymer MI

Fig. 12 shows the lap shear-test temperature relationships of three adhesives based on EMAAAs with MIs of 16, 160 and 345, respectively (Table I), crosslinked by a stoichiometric amount of diepoxy in the presence of 60 wt. % of rosin ester tackifier. The polymers have quite similar AA levels (7-11 wt. %). These formulated adhesives,

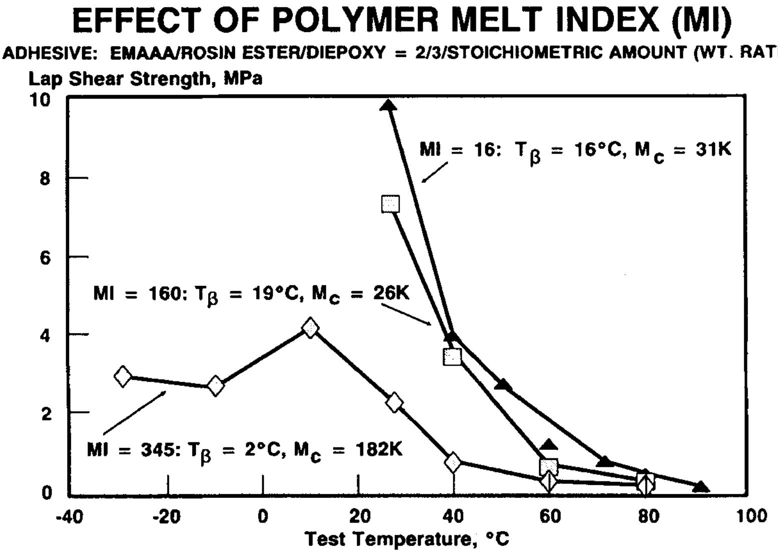


FIGURE 12 Lower polymer MI yields higher lap shear strength for crosslinked EMAAA adhesives.

after crosslinking, become totally amorphous. Adhesive T_β and M_c are shown. The strength of a crosslinked polymer should depend on M_c, primary molecular weight, and T_β. However, the effect of *MI* or primary molecular weight of the base polymer seems to override the effects of T_β and M_c on adhesive lap shear strength. Similar behavior was observed for crosslinked EAA and EVAVOH adhesives (Figs. 13 and 14).

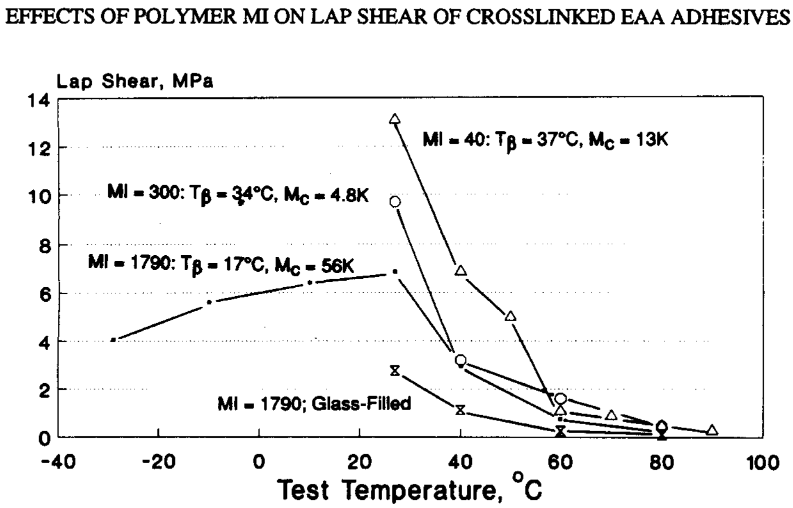


FIGURE 13 Lower polymer MI yields higher lap shear strength of the crosslinked EAA adhesives.

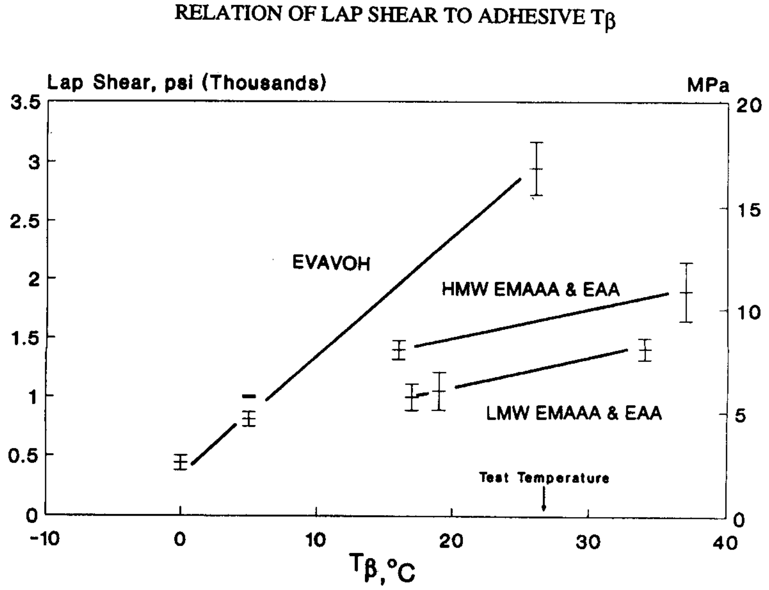


FIGURE 14 High adhesive T_β (low chain mobility) retards crack growth and delays adhesive fracture.

The strength of a system of network chains depends strongly on the primary molecular weight. This is due to the fact that the original polymer having number average molecular weight M_n before crosslinking contains $\rho N/M_n$ chains or $2\rho N/M_n$ chain ends, where N is Avogadro's number. Therefore, to a first approximation, each chain end will cause one of the network chains to be ineffective. Examples are chains *A* and *B* in Fig. 15. Also, any chain near an ineffective chain will only be partially effective. Chain *D* is an example because one of its ends is attached to a chain with a loose end. This holds true for chains *E*, *F*, and *G*. On the other hand, chain *C* is fully effective because both ends of this chain do not attach to any chain with a dangling end. Therefore, we speculate that a higher molecular weight base polymer produces a lower degree of chain end defects in the adhesive networks, hence, higher shear strength.

Most of the formulations in Figures 10, 12 and 13 fulfill the strength requirements of semi-structural adhesives for the automotive industry: 0.5 – 3.45 MPa at 80°C, and fail cohesively at all test temperatures.[6] Also, after the simulated salt spray tests, all the adhesive/steel bonds exhibit the cohesive failure mode upon lap shear rupture.

Comparison with Toughened Epoxy

Fig. 16 compares the shear performance of the crosslinked EHEMA adhesive with the crosslinked EVAVOH adhesive and a model toughened epoxy (diepoxy/ATBN/DICY = 20/4.0/1.1 in wt. ratio). Both polyolefin adhesives contain 40 wt.% polymer, 60 wt.% rosin ester and the crosslinking system of diepoxy/PMDA. The crosslinked EHEMA and EVAVOH adhesives show comparable lap shear strength with galvanized steel over a wide range of temperatures. Also, they out-perform the model

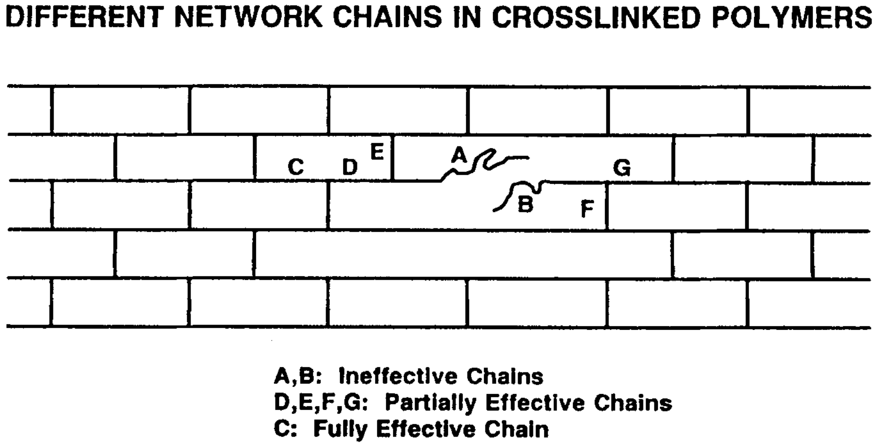


FIGURE 15 Lower primary molecular weight of base polymer → more chain end defects in crosslinked polymer → lower strength of network chains?

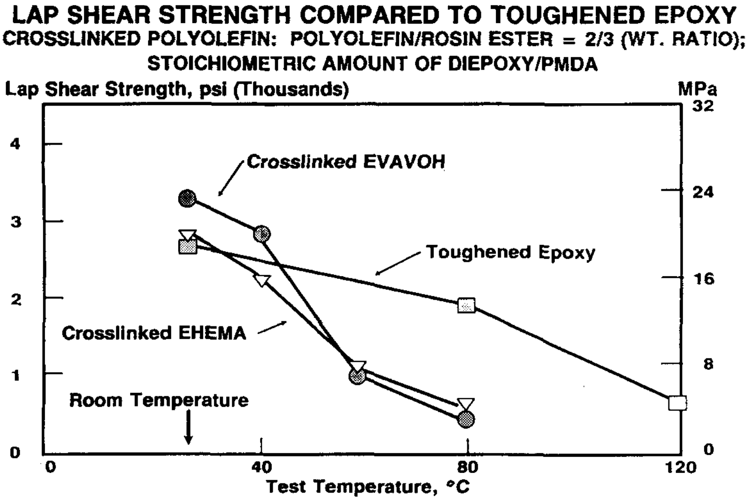


FIGURE 16 Crosslinked hydroxyl-containing polyolefins have higher room temperature lap shear strengths than toughened epoxy.

toughened epoxy at room temperature in terms of their lap shear strengths. More importantly, their 80°C lap shear strengths are up to 3 MPa, almost reaching the shear strength criterion for structural adhesives of 3.45 MPa for the automotive industry.[6] The comparison of environmental aging performance of crosslinked EVAVOH and EHEMA adhesives is shown in Fig. 17. Crosslinked EVAVOH retains about 45% of

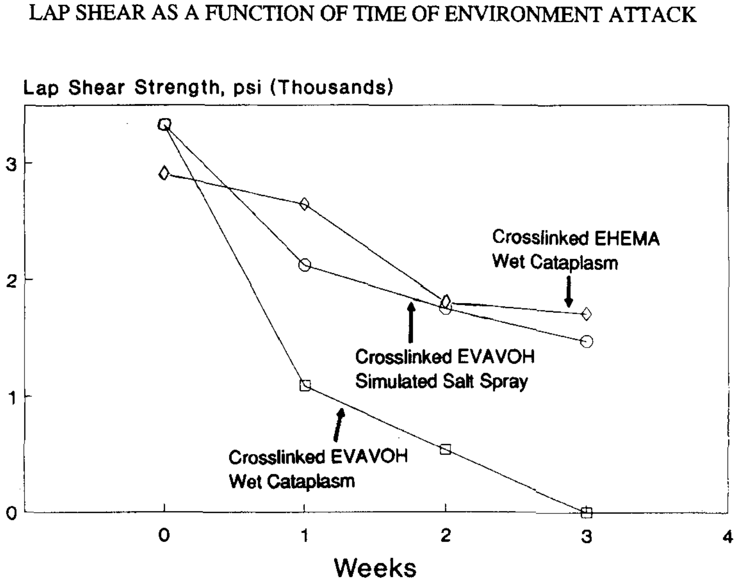


FIGURE 17 Crosslinked EHEMA exhibits better environment stability than crosslinked EVAVOH.

its original shear strength after 3 weeks of simulated salt spray, but fails miserably after 3 weeks of "wet cataplasm". On the other hand, crosslinked EHEMA is quite stable with a retention of at least 40–60% of its shear strength after the more severe "wet cataplasm" test. The locus of failure of the unaged lap joint is visually determined as cohesive for either the EVAVOH or EHEMA adhesive. After environmental attack, the fractured joint exhibits some degree of apparent interfacial failure (AIF) between the adhesive and the substrate.

Cure Kinetics

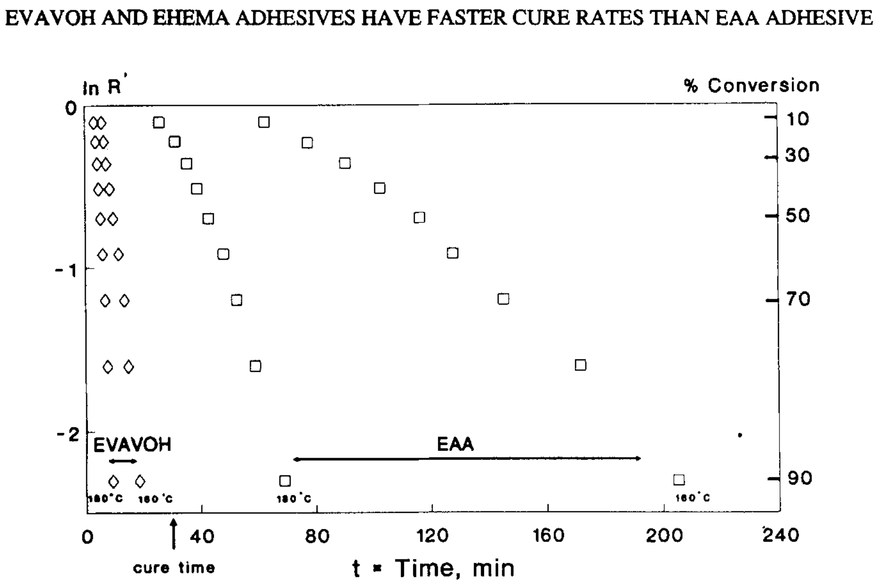
We have studied three different HMAs: crosslinkable EAA/rosin ester (EAA 2/rosin ester/diepoxy = 2/3/1.03 in wt. ratio), and the crosslinkable EVAVOH and EHEMA adhesives described in the last section. Our experimental results show that, in every case, the reaction rate, R', follows first order kinetics:

$$-d\ln R'/dt = k, \text{or} -dR'/dt = kR'$$

where t is the reaction time and k is the rate constant. k obeys the Arrhenius relation

$$k = A\exp(-E_a/RT)$$

where A is the frequency factor, R is the gas constant and T is the cure temperature in $^\circ K$. We compare the cure kinetics of the three polyolefin adhesives in Fig. 18. The



	EAA	EVAVOH	EHEMA
k Ratio	1	10	34
ln A, min^{-1}	21.2	19.8	15.4
E_a, kcal/mole	21.9	18.7	14.1

FIGURE 18 Cure kinetics of crosslinkable polyolefin adhesives studied by Monsanto Rheometer.

EHEMA adhesive cure rate is about 3.4 times faster than that of the EVAVOH adhesive. This could be explained by the nature of the hydroxyl group-secondary in EVAVOH but primary in EHEMA, and the longer, hydroxyl-bearing side chain of the HEMA structural unit. On the other hand, the EHEMA adhesive has a cure rate about 34 times faster than the EAA adhesive.

Relationship of Lap Shear to Adhesive Storage Modulus

Fig. 19 compares the variation of lap shear strength and storage modulus G' in the temperature range of $-30°$ to 80°C for the crosslinked EVAVOH adhesive. There is a concomitant drop of shear and G' near the adhesive's T_β. The correlation of log (shear) and log G' is shown in the small insert of Fig. 19. Notice that, due to the small differences in log (shear) and log G' of the two data points in the lowest temperature region, they are "clustered" together in this small insert. Therefore, lap shear appears to be proportional to G' to a power of 0.38.

By this same procedure, we arrive, in Fig. 20, at the log–log plots of shear *versus* G' for a diisocyanate-crosslinked EVAVOH adhesive (EVAVOH 1/Escorez 1310LC/ε– caprolactam blocked isophorone diisocyanate = 3/2/0.65 in wt. ratio), the model toughened epoxy, an epoxy crosslinked EMAAA adhesive (EMAAA 1/rosin ester/diepoxy = 2/3/0.36 in wt. ratio), and the crosslinked EHEMA adhesive. It appears that

$$\tau_f = K(G')^s, s = [0.38, 0.69] \qquad (1)$$

where s and K of these various semi–structural and structural adhesives are shown in Table II. Without direct evidence, we suspect that there may be a tackifier weak boundary layer at the interface of steel and the diisocyanate-crosslinked EVAVOH adhesive (Fig. 3), resulting in a stronger dependence on G' of τ_f for this adhesive. This

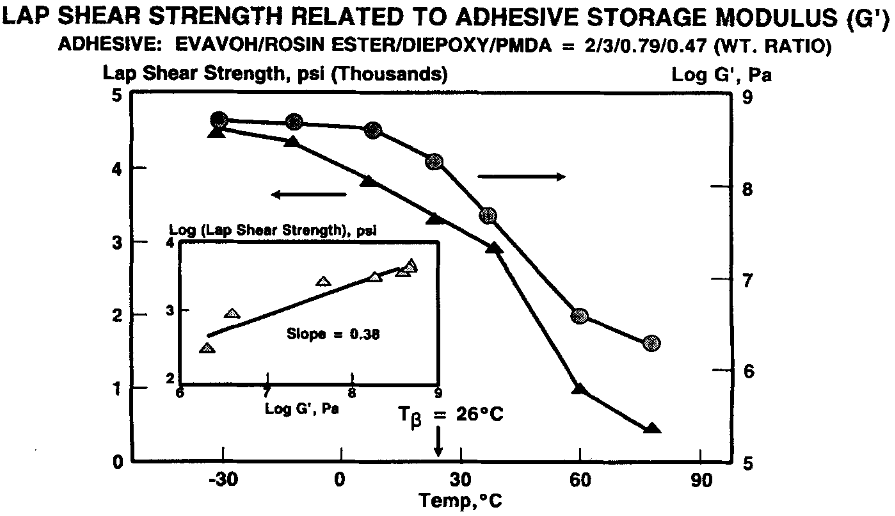


FIGURE 19 Concomitant drops of lap shear strength and storage modulus near T_β for crosslinked EVAVOH/rosin ester adhesive.

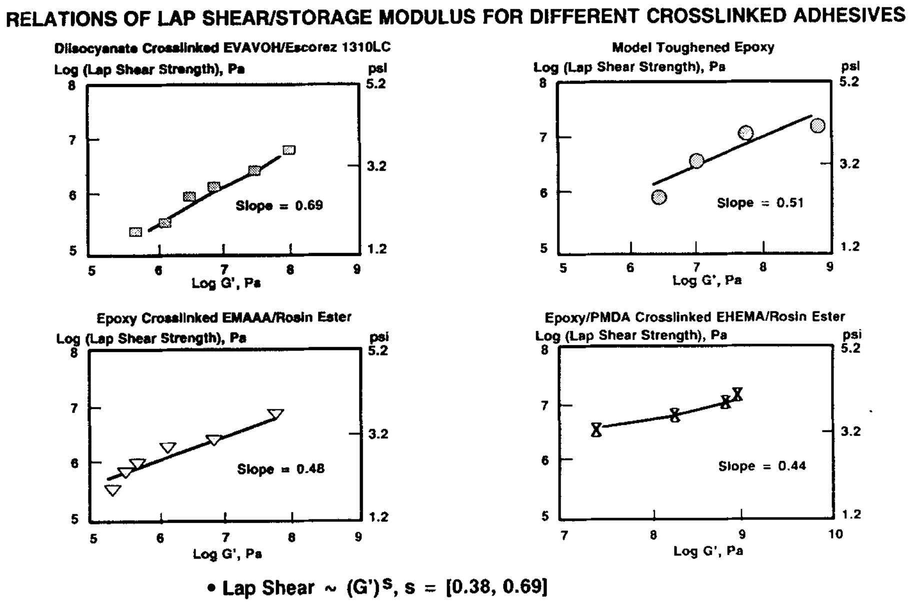


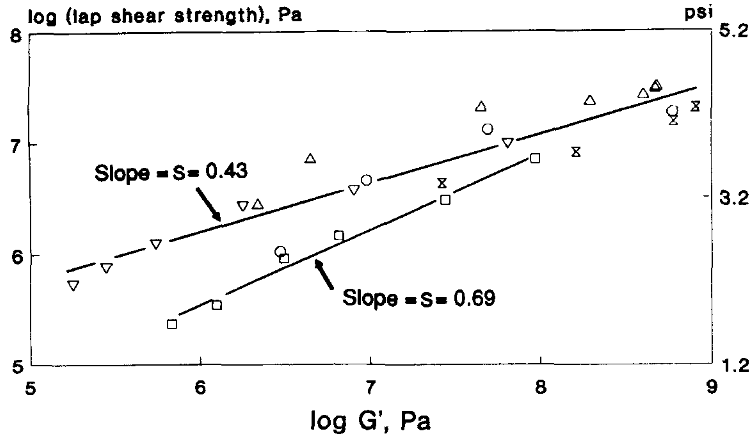
FIGURE 20 Lap shear increases with adhesive storage modulus for structural and semi-structural adhesives.

TABLE II
Fracture Energies, G_a of Adhesive Bonds Estimated from Linear Elastic Fracture Mechanics

Crosslinked Adhesive	s	K	LOF	G_a,J/m^2 Eq. 2	G_a,J/m^2 Eq. 3	n, bonds/nm^2 Eq. 2	n, bonds/nm^2 Eq. 3
EVAVOH/Escorez 1310LC	0.69	25.94	AIF	6.73×10^{-2}	1.06×10^{-2}	0.12	0.02
Toughened Epoxy	0.51	9.08×10^2	AIF	82.4	12.9	150	24
EMAAA/Rosin·Ester	0.48	2.12×10^3	CF	450	70.6	820	128
EHEMA/Rosin Ester	0.44	2.28×10^3	CF	520	81.6	945	150
EVAVOH/Rosin Ester	0.38	1.65×10^4	CF	2.72×10^4	4.27×10^3	49500	7800

adhesive fails mostly in the AIF mode at various test temperatures. Actually, when we combine all the data in Figures 19–20 in Fig. 21, the more compatible adhesive systems tend to form a group with a value of $s = 0.43$ (correlation coefficient = 0.933). The less compatible EVAVOH/Escorez 1310LC adhesive exhibits a somewhat different behavior with a value of $s = 0.69$ (correlation coefficient = 0.993). A value of $s = 0.51$ (correlation coefficient = 0.882) is obtained when the data of all 5 adhesives are combined.

Gent[7] analyzed the two extreme cases of the lap shear geometry in terms of the fracture energy per unit area detached, G_a. For incompressible, linearly-elastic



COMBINED LAP SHEAR/STORAGE MODULUS RELATIONS OF CROSSLINKED ADHESIVES

FIGURE 21 Dependence of lap shear on adhesive storage modulus for compatible and less compatible adhesive systems: symbols same as in Figures 19 and 20.

materials, the applied shear stress at break is

$$\tau_f = (2G_a G'/h_a)^{1/2} = 100(G_a G')^{1/2} \tag{2}$$

for adhesive layers having a relatively large debonded area (thin adhesives), or

$$\tau_f = (2G_a G'/\pi c)^{1/2} = 252(G_a G')^{1/2} \tag{3}$$

when the length, c, of debond is much smaller than h_a (thick adhesives). We arrive at the last equation by using the size of a surface flaw of 10^{-5} m.[8] To fit our experimental data, we simply assume s to be 1/2 in Equation (1). Then, from Equations (2) and (3), we have $G_a = 10^{-4}K^2$ (Thin Adhesives) and $G_a = 1.57 \times 10^{-5}K^2$ (Thick Adhesives), respectively. Of course, we also assume in Equations (2) and (3) that stress concentration effects in the immediate vicinity of the edge are negligible. Values of G_a of all five adhesives calculated from the last two equations are shown in Table II, where LOF, CF and n represent locus of failure, cohesive failure and the number of covalent bonds per unit interfacial area, respectively. Although we presently do not know the physical significance of the numbers representing G_a, their magnitudes seem to be in rough accord with the degree of interfacial bonding and locus of failure at the adhesive/steel interface. Larger values of G_a could possibly result from interfacial chemical bonding. The adhesive also fails cohesively in this case. Of course, some estimated G_a values are too low, whereas othere are too high (small values of G_a expected to be ~ 1–$10\,\mathrm{J/m^2}$; large values of $G_a \sim 10^3\,\mathrm{J/m^2}$). Also, no single value of c in Equation (3) gives all the above results reasonable values for G_a. This is possibly due to the reason that mechanics of failure may be different in various adhesive bonds. The n value is calculated by assuming a dissociation energy per covalent bond of 5.5×10^{-19} J. These values represent very rough estimates. For each adhesive in Table II, the G_a or n value is higher for the thin adhesive case than the thick adhesive case.

CONCLUSIONS

The major effort of this work is to determine if functionalized polyolefins could be formulated with tackifiers and epoxy to produce a crosslinkable hot melt adhesive. Conclusions based on this study are very supportive to these acid- or hydroxyl-containing olefinic polymers as promising candidates for use as semi-structural adhesives to bond oily galvanized steel surfaces in the automotive industry. Also, one key result of this study is that the lap shear strength of a galavanized steel joint of crosslinked adhesive depends on adhesive storage modulus to the power of roughly 1/2. A rough estimate of the fracture energy of the adhesive bond, G_a, could be obtained from this relationship. Although some estimated G_a values are too low while the others are too high, they seem to be in rough accord with the degree of interfacial bonding and the locus of failure of the lap shear bonds.

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