Adhesive Properties of DGEBA–Acid Homopolymer and DGEBA–Acid Copolymer Systems

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SYNOPSIS

Adhesive properties of high molecular weight acid copolymers used as hardeners for a commercial epoxy resin are investigated. For comparative purposes, physical blends of poly(acrylic acid)–polystyrene are used as hardeners. Joints prepared from physical blends exhibit lower lap shear strength than do those prepared from synthesis products. The use of copolymers is more adequate. Thermodynamic work of adhesion using wettability criteria is explored to explain the differences. The apparent energies of rupture determined by lap shear tests are 10^3 higher than those of the thermodynamic work of adhesion. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The objective of the present study was to evaluate different types of structural adhesives based on a commercial epoxy resin DGEBA and a polymer, poly(acrylic acid) (PAA), and copolymers, Poly(anhydride maleic)–styrene (PAMS) and poly(acrylic acid)–styrene (PAAS), at different contents of styrene as curing agents. The styrene gives to the adhesive the properties of mechanical resistance, whereas the acid or anhydride components provide for the cross-linking reaction.[1-2] The adhesive properties are obtained by the release of the OH function during the cross-linking reaction.

Copolymers with a preponderance of polystyrene (PS) have a higher apparent elasticity limit[3] under stress. The plastic yielding of the PS domains creates an energy-dissipation process that operates at high stresses and prevents brittle fracture.

For comparative purposes, physical blends of PAA/PS are used as hardeners. The association process via physical blending presents the advantage that it is more economical and easier than is copolymerization. The physical blends are phase-separated.[4]

EXPERIMENTAL

Polymers and copolymers are synthesized by free-radical polymerization in solution. Physical blends are prepared by dissolving them in a common solvent under continuous stirring. The average molecular weight in number $(\bar{M}_n)$ of the homopolymers used in the physical blends are 5500 and 7400, respectively, for PAA and PS.

The adhesive comprises of a mixture of the epoxy resin/copolymer in stochiometric proportions (1 mol acid/1 mol epoxy) in the presence of a tertiary amine. Triethylamine (TEA) was used as the catalyst for the cross-linking reaction. The substrates used were pure aluminum, lumber core plywood, and float glass.

Joint Preparation

The aluminum substrates were degreased in trichloroethylene; after drying, their surfaces were roughened by sandpaper. The chemical treatment was performed by immersion of the substrates in a chromic acid bath at 70°C for 15 min. The substrates were then rinsed in running tap water and finally in water at 60°C. The wooden substrate treatment consists of mechanical sandpaper roughening. Concerning the glass, the surface treatment was carried out by rinsing it with ethyl alcohol and drying it.

Table I   UV Results

CP Ref.	Copolymer Composition	
	% Styrene	% Acrylic Acid
CP 10	94	6
CP 25	84	16
CP 50	41	59
CP 75	28	72
CP 90	16	84

The assemblage consists of a simple overlap joint. The bonded areas were 4.06×10^{-4} m, 4.48×10^{-4} m, and 6.25×10^{-4} m for aluminum, plywood, and glass, respectively. A constant pressure is applied on the joint surface. Joints are then transferred into a ventilated dryer in order to activate the cross-linking. The activation parameters are 2 h and 100°C.

DETERMINATION OF THEORETICAL WORK OF ADHESION

The method, already well known, uses measurements of the contact angle of a series of liquids on the solid in the presence of their vapor. This method was described by Schultz and Gent[5] and was derived from Girifalco and Good,[6] Fowkes,[7] and Dann.[8]

The expression that gives, in the most general case, the contact angle of a liquid on a solid of weak superficial energies (polymers) is

$$\text{Cos } \theta_{SL_v} = 2(\gamma_S^D)^{1/2} \frac{(\gamma_L^D)^{1/2}}{\gamma_L} + \frac{I_{SL}^P}{\gamma_L} - 1 \qquad (1)$$

where θ_{SL_v} is the angle contact of the liquid on the solid in the presence of the vapor (v) of the liquid, γ_S^D, the dispersial component of the free energy of the solid, γ_L^D, the dispersial component of the free

Table II   GPC Results

CP Ref.	M_n	M_w	I
PAA	5,531	6,961	1.25
PAMS	41,675	48,672	1.17
CP 90	51,727	56,228	1.10
CP 75	49,879	56,642	1.14
CP 50	70,171	81,569	1.16
CP 25	81,494	93,245	1.50
CP 10	85,187	97,122	1.14

Table III   Lap Shear Strength on Wood/Wood Assemblies

Copolymers/DGEBA	MPa
Poly(anhydride maleic)–styrene (PAMS 50)	2.00 ± 0.20
Poly(acrylic acid) (PAA)	2.02 ± 0.23
Poly(acrylic acid)–styrene (PAAS)	
CP 90	1.12 ± 0.38
CP 75	1.70 ± 0.21
CP 50	2.11 ± 0.32
CP 25	2.30 ± 0.30
CP 10	3.40 ± 0.20

energy of the liquid, γ_L, the free superficial energy of the liquid, and I_{SL}^P, the polar interaction forces.

The measurement of the contact angle of the series of liquids allows determination of the surface energy of the adhesive. The measurement of the contact angle (θ) is done by measuring the dimensions of the liquid drop deposed on the solid surface (adhesive) using the single formula.[9] The considered adhesives are PAMS 50/DGEBA and CP 50/DGEBA.

APPARATUS

Infrared spectroscopy was performed on a PYE UNICAM series SP3 spectrophotometer. The composition, i.e., the real percent of styrene and acrylic

Table IV   Lap Shear Strength on Al/Al Assemblies

Copolymers/DGEBA	MPa
Poly(anhydride maleic)–styrene (PAMS 50)	5.8 ± 0.3
Poly(acrylic acid) (PAA)	7.4 ± 0.4
Poly(acrylic acid)–styrene (PAAS)	
CP 90	2.4 ± 0.2
CP 75	2.5 ± 0.1
CP 50	3.2 ± 0.05
CP 25	3.7 ± 0.2
CP 10	4.1 ± 0.3
PAA/PS/DGEBA (Blend)	MPa
PAA/PS 90/10	0.8 ± 0.2
PAA/PS 75/25	0.6 ± 0.2
PAA/PS 50/50	0.5 ± 0.3
PAA/PS 25/75	1.4 ± 0.1
PAA/PS 10/90	0.9 ± 0.1

acid in the synthesis products, was determined by uv spectroscopy. The UV measurements were performed in THF solution in the range of 200–300 nm. Molecular weights were determined by GPC in THF solution using an instrument with Styrogel columns and a differential refractometer. An Instron mechanical tester Model 1195 was used to perform the lap shear tests according to ASTM D 1002 at a crosshead speed of 50 mm/mn.

RESULTS AND DISCUSSION

The UV results are presented in Table I; the GPC results appear in Table II.

The experimental results relative to the lap shear strength for wood/wood and aluminum/aluminum assemblies are given in Tables III and IV. Table V presents the literature results. As far as the glass assemblies are concerned, the mechanical properties of the glass used are poor; the destruction of the assembly is due to the support rupture.

We observed that for Al/Al assemblies at 100% of acrylic acid, the lap shear strength was the highest. The lap shear strength decreases considerably when we used PAAS copolymers; then, it increases with an increasing percent of styrene content. The same phenomenon is observed on wood/wood as-

Table V   Lap Shear Strength from the Literature

Triblock polymer:
polystyrene–polyisoprene–polystyrene[10]

% PI	Al	Wood
	(MPa)	
12.7	2.91	2.87
24.8	2.18	1.34
49.6	1.99	1.07
67.0	1.98	1.44

Polyamide nylon 6/novolac (formaldehyde Phenol)[11]

Proportions	Wood (MPa)
10/90	2.8
23/77	2.7
50/50	3.5
44/56	1.8
41/59	1.0

Table VI   Superficial Energies of the Liquids Used

Liquid	γ_L	γ_L^D	γ_L^P
Water	72.2	22.2	50.0
Ethanol–Water			
10/90	51.3	20.0	31.3
20/80	42.0	19.0	23.0
30/70	36.1	18.5	17.6
50/50	30.0	17.7	12.3
70/30	27.2	17.6	9.6
90/10	24.0	17.2	6.8
Ethylene–glycol	50.8	48.5	2.3

γ_L, γ_L^D, and γ_L^P in $J/m^2 \times 10^{-3}$.

semblies, but the lap shear strength at 100% of acrylic acid is fairly equal to that of CP 50.

We hypothesize that when the PS content increases in the PAAS copolymer, it forms a continuous glassy phase that reinforces the structure copolymer and increases the energy of rupture. The alternating copolymers (PAMS) present a better regularity in their structure than do the statistical copolymers (PAAS); this gives them a better stress distribution.

The molecular weight effect is important; in fact, the adhesion is an inverse function of the molecular mass[12]: the lower the mass, the better will be the penetration of the glue in the microcavities, allowing, thus, an increase in the number of van der Waals bonds, which increases the adhesivity. The average molecular weight in number ($\bar{M}_n$) of PAMS 50 is lower than the average molecular weight in number of CP 50 (see Table II).

This can be applied to the adhesive joints prepared for PAA polymers that give a higher lap shear strength than those prepared from PAAS copolymers. The $\bar{M}_n$ of PAA is lower than that of PAAS.

Another effect of primary importance is that of cohesion. Acrylic acid is a very flexible molecule; it is a better adhesive than the PS molecule, which is inflexible. This is explained by the secondary van der Waals bond that gives rise to an attraction between molecules, resulting in better cohesion. This cohesion can be observed in the failure mode of the wood/wood assemblies where there is no molecular weight effect; wood substrates present a high porosity, allowing, thus, a high penetration of the glue in the case of high and low masses.

In the case of a joint prepared from the PAA polymer, all the failures take place in the wood. The adhesive presents a good cohesion. Furthermore, in joints prepared from PAMS, 95% of failure takes

Table VII Angle Contact of Different Liquids on CP 50/DGEBA and PAMS 50/DGEBA Adhesives

Liquid	$(\gamma_L^D)^{1/2}/\gamma_L$	CP 50/DGEBA		PAMS 50/DGEBA	
		θ	Cos θ	θ	Cos θ
Water	0.065	100.77	−0.187	107.33	−0.298
Ethylene–glycol	0.112	84.77	0.091	70.00	0.342
Ethanol water					
10/90	0.087	83.51	0.113	88.54	0.0254
20/80	0.104	84.20	0.101	71.08	0.324
30/70	0.119	75.52	0.250	46.05	0.694
50/50	0.140	54.41	0.596	36.77	0.801
70/30	0.154	42.94	0.732	17.63	0.953
90/10	0.173	27.74	0.885	20.60	0.936

place in the wood. The structure of alternating co-polymer presents a better regularity, which results in a high cohesion.

Likewise, we observe that Al/Al assemblies present a higher lap shear strength than that of wood/wood assemblies. A pure-state aluminum has a higher energy surface than that of wood (2000 mJ/m^2 for metal and 200 mJ/m^2 for wood).[13]

Joints prepared from physical blends present a lower lap shear strength than those prepared from synthesis products. A recent study[4] proved the incompatibility of the blend PS/PAA. This incompatibility results in a weak cohesion and weak joints.

Comparing the adhesive joints prepared from synthetized copolymers and polymers to the literature results,[10,11] we observe (refer to Table V), that our formulations have a lap shear strength fairly equal to those of nylon 6/novolac blends used as structural adhesives, whereas they are performed better than does the triblock polymer of polystyrene–polyisoprene–polystyrene adhesives.

THEORETICAL WORK OF ADHESION

Table VI gives the superficial energies of different liquids. Table VII gives the angle contact of different liquids on the considered adhesives.

Figures 1 and 2 are represented by the variation of Cos θ vs. the quantity $(\gamma_L^D)^{1/2}/\gamma_L$ characteristic of the liquid used. In the two cases, the experimental points follow the general eq. (1). The curves do not pass by the origin. The term I is not nul. In the vicinity of Cos $\theta = 1$, the values of γ_L^P liquids used are weak and, therefore, the interaction of polar type I can be considered as negligible. The intersection of these curves with the axis Cos $\theta = 1$ allow determination of the surface energy of the adhesives.

Table VIII gives the comparative results between the theoretical energy of adhesion and the energy of rupture. The apparent energies of rupture determined by the lap shear test are 10^3 higher than is the reversible energy of adhesion. This is in agreement with the literature.[14] This difference in the
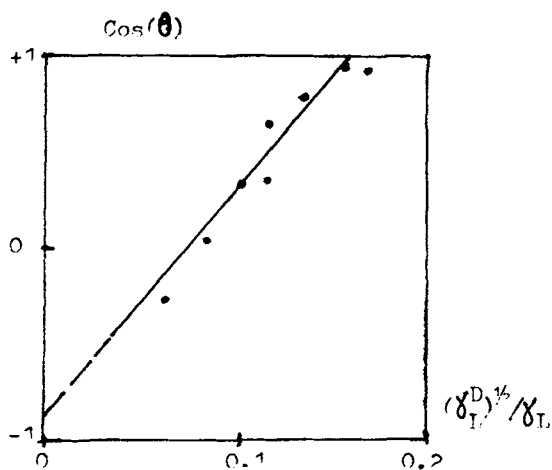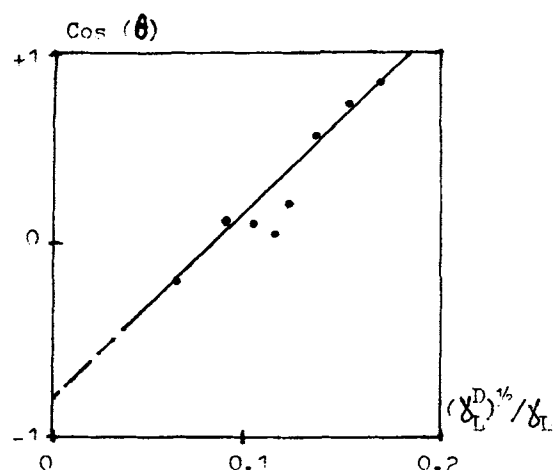

Figure 1 PAMS 50/DGEBA Adhesive.

Figure 2 CP 50/DGEBA Adhesive.

Table VIII   Apparent Energy of Rupture and Reversible Energy of Adhesive for the Adhesives CP 50/DGEBA and PAMS 50/DGEBA

Apparent Energy of Rupture (J/m² 10³)				Thermodynamic Work of Adhesion (J/m²)			
CP 50/DGEBA		PAMS 50/DGEBA		CP 50/DGEBA		PAMS 50/DGEBA	
Al	Wood	Al	Wood	Al	Wood	Al	Wood
0.480	0.315	0.855	0.300	0.490	0.155	0.559	0.177

order of magnitude has initiated a great number of studies aimed at the establishment of a significant relationship between the measured strength of the adhesive system and its theoretical strength calculated based on the molecular interactions. Some of these works[15-18] have resulted in qualitative correlations between the strength of adhesive bond and thermodynamic values proper to solids in contact, such as the wetting superficial energy and the contact angle.

The work required to break an adhesively bonded joint has been regarded as the sum of several contributions:

1. Thermodynamic surface energies, arising from dispersion forces or chemical bonds acting across the interface.
2. The mechanical energy dissipated by irreversible deformation processes within the adhesive itself.
3. Similar energy dissipation within the adherent during detachment.

We notice that factor I is neglected in our theoretical calculation due to the nonexistence of a relationship among I_P, γ_L, and γ_S, but we estimate that the difference of polarity between the substrate and the adhesive should not be neglected.

CONCLUSIONS

Our research relative to the adhesive properties has allowed us to determine the performances of these adhesives:

- Joints prepared from physical blends exhibit lower lap shear strength than that of those prepared by synthetized products.
- The best performing joints were obtained from acrylic acid–styrene copolymers with a lower content of acrylic acid (CP 10 and CP 25).

- The alternating copolymers of maleic anhydride–styrene exhibit a higher adhesion and a better shearing behavior than those of the statistical copolymers, especially in the case of Al/Al substrates.
- Al/Al substrates exhibit a higher lap shear strength than that of wood/wood substrates. This allowed us to deduce that our formulations are adequate for glass and metal substrates.

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