Polyester Hot-Melt Adhesives.   I.   Factors Affecting Adhesion to Epoxy Resin Coatings*

W. J. JACKSON, JR., T. F. GRAY, JR., and J. R. CALDWELL, *Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee 37662*

Synopsis

The peel strength and tensile shear strength of polyester hot-melt adhesives on metals coated with epoxy resins are affected by four characteristics of the polyester: (1) inherent viscosity, (2) glass transition temperature (T_g), (3) degree of crystallinity, and (4) melting point.   The inherent viscosity affects the strength, toughness, and crystallinity of the adhesive.   The T_g and degree of crystallinity affect the low-temperature adhesive properties; the peel strength is relatively low when the T_g is appreciably above the use temperature.   The T_g, degree of crystallinity, and melting point affect the high-temperature adhesive properties.   A hot-melt adhesive with high peel and tensile shear strengths from 0° to 120°C is the polyester of 1,4-butanediol and *trans*-1,4-cyclohexanedicarboxylic acid.

INTRODUCTION

Because loss of heat is all that is necessary for bond formation by hot-melt adhesives, bond formation occurs much more rapidly than with most other types of adhesives and thus permits high production speeds.[1]   An important application is the bonding of metals coated with epoxy resins, such as the side seams of cans.[2,3]   The inert resin protects the contents of the can from possible reaction with the metal.   In this application, heat resistance is also necessary, depending upon the contents of the can; for example, beer is pasteurized at 70°C and many foods are sterilized at 120°C.

Polyesters vary considerably in their adhesion to metals and to metals coated with epoxy resins.   The objective of this investigation was to determine the polyester characteristics which affect adhesion to epoxy resin-coated metals.   In a subsequent paper, the adhesion of polyesters to metals will be discussed.

EXPERIMENTAL

Materials

All of the polyesters of the nonaromatic diols were prepared by conventional procedures from the diols and dialkyl esters of the dicarboxylic

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acids,[4,5] and the polyesters of bisphenol A (4,4'-isopropylidenediphenol) were prepared from bisphenol A diacetate and the free dicarboxylic acids.[6] Their inherent viscosities (IV) were measured at a concentration of 0.25 g/-100 ml in a 60/40 phenol/tetrachloroethane mixture at 25°C.

The adhesive bond strengths listed in Tables I to V were obtained with commercial epoxy phenolic-coated 8-mil aluminum can stock and with epoxy phenolic-coated 6.5-mil chrome-coated steel can stock.

Bond strengths also were obtained after we applied an epoxy phenolic coating on 8-mil aluminum can stock and on 6.5-mil chrome-coated steel (Weirchrome can stock obtained from Weirton Steel Co.). The metal sheets were cut to give 1- × 5-in. specimens, which were washed three times with a solution of Alconox detergent, rinsed in water each time, rinsed in acetone, and dried. The specimens were then dipped into M and T Primer XL3680 (M and T Chemicals, Inc.) diluted with M and T Thinner XL-3680-T to give 14% solids. After the suspended specimens had been dried, they were heated for 15 min in an oven at 215°C to cure the coating.

Bond strengths were also determined with several representative polyesters when the metal specimens were coated with an unmodified bisphenol A polyepoxide. The cleaned specimens were dipped into a solution consisting of 10 g of Epon 828 (Shell Chemical Co.), 70 ml of chloroform, and 0.3 g of diethylenetriamine (catalyst). After the coating had dried, it was cured in an oven at 200°C for 1 hr.

Adhesive Bond Formation and Testing

Just before use, the polyepoxide-coated specimens were sprayed with acetone and allowed to dry. A hot plate whose surface temperature could be adjusted to any desired value ±2°C was used to heat the specimens for bond formation. The temperature used was high enough for the polyester to melt when applied as particles. A hot plate temperature of 240°–260°C was used for most of the polyesters, but higher temperatures were required for the highest melting polyesters (280°C for the polyterephthalates of 1,3-propanediol and 1,4-butanediol, 300°C for the polyterephthalates of ethylene glycol and 1,4-cyclohexanedimethanol, and a metal bath at 320°C for the polyesters of bisphenol A and 2,2,4,4-tetramethyl-1,3-cyclobutanediol).

For T-peel tests, the molten polymer was evenly spread on the heated specimen over a 2-in. length with a wooden spatula. The second coated specimen was pressed against the sample, and then the laminated sample was turned over on the hot plate with the second specimen against the surface of the hot plate. Heating was continued while the wooden spatula was rubbed back and forth over the adhesive area until a smooth, even glue line was obtained (about 30 sec). Then the bonded sample was placed on the Alberene stone benchtop and rubbing was continued for about 20 sec longer while the adhesive cooled. Glue lines were about 5 mils thick. The T-peel strengths of the laminates were measured with an Instron tensile

TABLE I
Adhesive Strength of Terephthalate Polyesters

Polyester Diol constituent	IV	T_p, °C	Relative cryst., %	T-Peel strength[a] at 23°C, lb/in. width	Tensile shear strength,[b] psi 23°C	Tensile shear strength,[b] psi 70°C
Ethylene glycol	0.63	69	0	1	>2000[c]	1700
1,3-Propanediol	1.12	35	17	1	>2000[c]	1200
1,4-Butanediol	0.88	30[d]	28	1	2000	1600
2,2-Dimethyl-1,3-propanediol	0.77	68	0	1	>2000[c]	1200
1,4-Cyclohexanedimethanol (70% *trans*)	0.83	85	12	1	>2000[c]	900
2,2,4,4-Tetramethyl-1,3-cyclobutanediol (60% *trans*)	0.69	184	0	0	1900	—
Bisphenol A[e]	0.95	197	0	1	>2000[c]	>2000[c]

[a] Substrate is epoxy phenolic-coated 8-mil aluminum.
[b] Substrate is epoxy phenolic-coated 6.5-mil chrome-coated steel.
[c] Metal failed; adhesive bond held.
[d] Value may be somewhat high because of the presence of crystallinity.
[e] Since the polyterephthalate has a very high melting point, the 50/50 terephthalate/isophthalate copolymer was used.

tester by the general method of ASTM D1876-61T, but using the precut specimens. A forced-air oven was fitted around the tester for determinations at elevated temperatures.

For tensile shear tests, the adhesive bonds were formed by the same general procedure but with 0.25-in. overlap. The tensile shear strengths were measured with the Instron tensile tester by the general method of ASTM D1002-64, but using the precut specimens. These methods of forming the adhesive bonds gave very reproducible results when the same hot-plate temperature was used. Temperatures which were 20°C or more lower gave lower peel strengths with some polyesters because of poorer wetting of the specimens by the adhesive; temperatures which were 20°C or more higher sometimes gave lower peel strengths because of oxidation or breakdown of the polyester. In general, temperatures of 240° to 260°C were optimum when the adhesive flowed sufficiently to wet the specimens adequately.

Glass Transition Temperature, Melting Point, and Degree of Crystallinity

Glass transition temperatures were determined with a Perkin-Elmer Model DSC-1 differential scanning calorimeter (DSC). Thin films, prepared from the polymer melt on a hot plate, were heated in the aluminum DSC sample pan about 25° to 50°C above their melting points and then rapidly quenched by cooling on a metal plate at room temperature. Samples which were not obtained in the amorphous state by this treatment were quenched on a steel block which had been cooled to the temperature of liquid nitrogen. (Even this treatment was not sufficient to quench the 1,4-butanediol polyesters of terephthalic acid and *trans*-1,4-cyclohexane-dicarboxylic acid.) The samples were then placed in the DSC at tempera-

TABLE II
Peel Strength of Modified Poly(ethylene terephthalates)

| | | Polyester | | | T-Peel strength,[a] lb/in. width | |
| | | | | Relative cryst.,[c] | | |
Example	Acid constituents[b]	IV	T_g, °C	%	23°C	70°C
1	terephthalic (T)	0.63	69	0	1	5
2	75/25 T/adipic	0.66	34	0	4	17
3	70/30 T/adipic	0.54	21	0	15	7
4	67/33 T/adipic	0.49	15	0	45	5
5	85/15 T/azelaic	0.87	44	0	3	21
6	80/20 T/azelaic	0.77	28	0	1	17
7	75/25 T/azelaic	0.73	22	0	32	3

[a] Substrate is epoxy phenolic-coated 8-mil aluminum.

[b] Ratios of acid constituents are molar.

[c] All of the samples crystallized on heating in the DSC (20°C/min) up to the melting points. Crystallization took place between 100°C and 145°C, and melting points ranged from 170°C (example 4) to 247°C (example 1).

tures below their T_g's, and the thermograms were obtained at maximum sensitivity (4 mcal/sec full-scale deflection) with a programmed temperature rate of 20°C/min. The T_g was taken as the initial shift of the specific heat curve.

To determine the melting point and percentage of crystallinity, weighed film samples were melted as above, held in the melt for 1 min and then, to simulate the cooling rate when the adhesive bonds were prepared, quenched by cooling on a metal plate at room temperature. The cooled sample was then replaced in the DSC at 23°C and heated at a rate of 20°C/min back above the melting point, indicated by the endothermic peak.

The area of the melting peak was measured with a planimeter and compared with the peak area of indium metal (known weight and heat of fusion) to determine the heat of fusion of the sample.[7] The percentage of crystallinity was then calculated by comparing the heat of fusion with that of 100% crystalline poly(tetramethylene terephthalate), 7600 cal/monomer unit, or 36.5 cal/g.[8] The formation of an exothermic peak on the thermogram during the heating cycle indicated that crystallization took place on heating, and the percentage of this crystallinity was subtracted from the percentage of crystallinity determined from the melting peak to give the amount of crystallinity present in the quenched sample.

RESULTS AND DISCUSSION

Epoxy Resin Coating

All the adhesive values reported in Tables I to V were obtained with commercial epoxy phenolic-coated metals. Similar results with several representative polyesters were obtained when either an epoxy phenolic coating or an unmodified bisphenol A polyepoxide coating was applied to the metal. These adhesion values also were similar to those obtained with the commercial epoxy phenolic-coated metals.

Polyester Properties Which Affect Adhesion

In general, the polyesters had high tensile shear (lap shear) strengths on epoxy phenolic-coated and polyepoxide-coated aluminum and steel. At room temperature, the bonds (0.25-in. overlap) were usually stronger than the 8-mil coated aluminum (>1200 psi) and 6.5-mil coated steel (>2000 psi). Since steel is stronger than aluminum and higher tensile shear values can be obtained before the metal fails, these values for the terephthalate polyesters are listed in Table I. Metal failure is not a problem in measurements of peel strength, and the T-peel strengths in Tables I to IV were determined with epoxy phenolic-coated 8-mil aluminum. Peel strengths not greatly different were obtained when the coated metal was 7- to 8-mil tin-free steel. Similar or somewhat higher values were obtained when the epoxy phenolic-coated metal was 6.5-mil chrome-coated steel.

TABLE III

Peel Strength of 1,4-Butanediol Polyesters

| Example | Acid constituents[b] | Polyester | | Relative cryst., % | | | T-Peel strength,[a] lb/in. width | |
		IV	T_g, °C	23°C	Increase on heating[c]	T_m, °C	23°C	70°C
1	I	1.01	17	0	0	—	7	1
2	T	0.88	30[d]	28	0	224	1	—
3	T	1.15		22	0	224	9	11
4	90/10 T/H	1.03	20	26	0	209	4	2
5	80/20 T/H	0.99	16	20	0	194	5	6
6	70/30 T/H	1.06	7	16	0	174	12	34
7	60/40 T/H	0.98	4	0	12[e]	154	31	28
8	50/50 T/H	1.05	4	0	5[f]	132	68	30
9	40/60 T/H	1.04	4	<5	0	129	37	20
10	H	1.14	−11	0	0	—	31	1
11	C	0.60	−10	24	0	170	1	—
12	C	0.80	−10	21	0	167	32	25

13	C	1.13	−10	19.5	0	167	35	33
14	C	1.43	−10	17	0	163	35	34
15	70/30 C/T	0.72	0	22	0	161	6	14
16	70/30 C/T	1.10	0	17	0	166	35	37
17	60/40 C/T	0.57	2	24	0	172	1	—
18	60/40 C/T	0.86	2	17	0	164	26	35
19	50/50 C/T	0.62	11	20	0	174	1	15
20	50/50 C/T	1.57	11	15	0	169	21	35
21	80/20 C/H	0.99	−9	16	0	143	43	37
22	70/30 C/H	1.12	−10	15	0	133	60	34
23	80/20 T/A	0.71		20	0	194	3	3
24	60/40 T/A	1.14	−25	30	0	151	28	2

a Substrate is epoxy phenolic-coated 8-mil aluminum.

b Ratios of acid constituents are molar; I = isophthalic acid; T = terephthalic acid; H = 50/50 cis-/trans-1,4-cyclohexanedicarboxylic acid (hexahydroterephthalic acid); C = trans-1,4-cyclohexanedicarboxylic acid; A = azelaic acid.

c Increase in crystallinity in heating sample back to melting point (20°C/min heating rate) after sample had been melted and rapidly cooled to 23°C.

d Value may be somewhat high because of crystallinity.

e Crystallized at 43°–76°C (peak at 54°C).

f Crystallized at 57°–89°C (peak at 73°C).

TABLE IV
Peel Strength of *trans*-1,4-Cyclohexanedicarboxylate Polyesters

| Polyester | | | | T-Peel strength,[a] lb/in. width | |
Diol constituent	IV	T_g, °C	Relative cryst., %	23°C	70°C
Ethylene glycol	0.84	18	0	23	1
1,3-Propanediol	0.91	−6	0	13	1
1,4-Butanediol	1.13	−10	19.5	35	33
2,2-Dimethyl-1,3-propanediol	1.06	30	5	35	17
1,4-Cyclohexane-dimethanol	0.52	52	0	1	24
2,2,4,4-Tetramethyl-1,3-cyclobutanediol	0.77	169	0	1	—
Bisphenol A	1.09	150	0	1	—

[a] Substrate is epoxy phenolic-coated 8-mil aluminum.

Even though the terephthalate polyesters listed in Table I had high tensile shear strengths, they had very low peel strengths. Since the main problem was achieving high peel strength, much of the discussion will be concerned with this property and the tensile shear strengths are not listed in Tables II to IV. Wetting of the substrate did not appear to be a problem, because high tensile shear strengths were obtained. Lack of adequate flexibility in the polyester adhesive bond could cause the peel strength to be low, however. The glass transition temperature (T_g) is one measure of the flexibility of a polymer, and these values are listed in Table I. It is noteworthy that all of these T_g's are above room temperature (23°C).

Table II shows the effect on the peel strength when poly(ethylene terephthalate) was modified to reduce its T_g. The polymers with the highest peel strength at 23°C are those with T_g's below 23°C. Since noncrystalline polymers above their T_g's and below their flow points are rubbery and flexible, the polyesters with T_g's above 23°C and below 70°C had higher peel strengths at 70° than at 23°C. All the polyesters listed in Table II were noncrystalline when the molten polymer was rapidly cooled (the procedure used in preparing the adhesive bonds). Since noncrystalline polymers with T_g's below 23°C have low cohesive strength at 70°C, they have low peel and tensile shear strengths at 70°C as shown by examples 4 and 7.

To achieve flexibility and temperature resistance, a polyester must have a low T_g and some degree of crystallinity. For polymers other than poly(tetramethylene terephthalate), the crystallinity values (determined by DSC) in the tables are only approximate; but since the polyesters are similar in structure to poly(tetramethylene terephthalate), the values are approximations which were compared relative to each other.

It is important that the crystallization rate be rapid during adhesive bond formation. It is also important that the amount of crystallinity does

TABLE V
Tensile Shear Strength of 1,4-Butanediol Polyesters

| | Polyester | | | | | Tensile shear strength,[a] psi | | | |
Example	Acid constit- uents[b]	IV	T_g, °C	Relative cryst., %	T_m, °C	0°C	23°C	70°C	120°C
1	H	1.14	−11	0	—	>2400[c]	900	0	—
2	C	1.13	−10	19.5	167	>2400[c]	>2000[c]	>2000[c]	1500
3	80/20 C/H	0.99	−9	16	143	>2400[c]	>2000[c]	>2000[c]	600
4	60/40 C/T	0.86	2	17	164	>2400[c]	>2000[c]	>2000[c]	1100
5	T	0.88	30[d]	28	224	1500	2000	1600	600
6	T	1.15		22	224	>2400[c]	>2000[c]	>2000[c]	1000

[a] Substrate is epoxy phenolic-coated 6.5-mil chrome-coated steel.
[b] Ratios are molar; H = 1,4-cyclohexanedicarboxylic acid (50/50 cis/trans mixture); C = trans-1,4-cyclohexanedicarboxylic acid; T = terephthalic acid.
[c] Metal failed; adhesive bond held.
[d] Value may be somewhat high because of crystallinity.

not increase after bond formation, because strains are introduced and the bond strength is reduced. By use of the DSC, crystallization during heating can be determined. If any crystallization takes place when the rapidly cooled sample is heated back to its melting point, an exothermic peak in the DSC thermogram is obtained, and the amount of crystallization can be calculated. If no exotherm is obtained, the endothermic melting peak is a measure of the crystallinity formed when the molten sample was cooled initially. It should be noted that, even though crystallization does not take place under these conditions, it can occur on extended heating at an elevated temperature.

All of the polyesters listed in Table II were noncrystalline under the conditions used in forming the adhesive bonds, but they did crystallize on heating in the DSC instrument. In contrast, a polymer which crystallized rapidly and did not increase in crystallinity on heating was the polyester of terephthalic acid and 1,4-butanediol (Table III). Apparently because of its T_g (ca. 30°C) and crystallinity, the peel strength was low (examples 2 and 3). It was thought possible to improve the peel strength by modifying the polymer to reduce its T_g and crystallinity. Since the polyester of 1,4-cyclohexanedicarboxylic acid (50/50 *cis/trans* mixture) and 1,4-butanediol (example 10) had no crystallinity and a very low T_g (-11°C), copolymers of this acid with terephthalic acid and 1,4-butanediol were prepared (examples 4 to 9). They had intermediate T_g's and degrees of crystallinity between those of the two homopolymers. Unfortunately, the copolymers with the highest peel strengths (examples 7 to 9) had little or no crystallinity under the conditions used for making the adhesive bonds. The polyester of example 7 did develop a significant amount of crystallinity on heating to 70°C, but because of this, peel strength decreased greatly (to 5 lb/in. width at 23°C after the bonded specimens has been heated in an oven at 70°C for 30 min).

A polymer with more promising characteristics is the polyester (I) of 1,4-butanediol and *trans*-1,4-cyclohexanedicarboxylic acid. It has a low T_g (-10°C), crystallizes very rapidly when the adhesive bonds are made, does not change in crystallinity during the heating cycle or during 24 hr at 70°C, and gives high peel strengths at 23 and 70°C (examples 12 to 14 of Table III). The degree of crystallinity of the adhesive bonds decreases

I
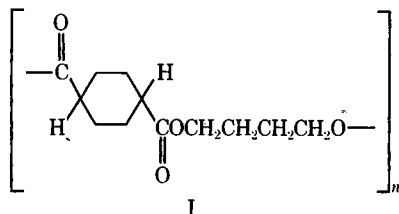
as the IV (inherent viscosity) of the polyester increases. Presumably, this decrease is caused by the increase in melt viscosity at the higher IVs. An IV of at least 0.8 appears to be desirable for polyester I, so that the level of

crystallinity is no more than about 21% and good peel strength can be obtained (examples 11 to 14 of Table III). When the polyester is non-crystalline, however, high peel strengths can be obtained with IVs as low as 0.5 (example 4 of Table II). Polyesters with appreciably lower IVs have insufficient cohesive strength to have good adhesive strength.

The interrelationship of IV, percentage of crystallinity, T_g, and peel strength of polyester I modified with terephthalic acid is shown in examples 15 to 20 of Table III. With each of the three compositions, the copolymer with the higher IV has the lower amount of crystallinity and the higher peel strength. The composition with the lower T_g (examples 15 and 16) has the higher peel strength also. Copolymers 21 and 22 have amounts of crystallinity similar to that of copolymer 20 but appreciably lower T_g's and appreciably higher peel strength. The amount of crystallinity that can be tolerated so that high peel strength is still attained depends upon the T_g; higher levels of crystallinity can be tolerated at lower T_g's (example 24). Lower T_g's are an indication of increased flexibility of the polyester chains, which offsets the stiffening effect produced when the crystallinity is increased. Bond flexibility must be maintained because it is necessary for high peel strength.

The crystalline melting point of the polyester (T_m in Table III), in conjunction with the degree of crystallinity, controls the upper temperature limit of the adhesive. The T_g affects the lower temperature limit. Polyester I modified with 40 mole-% of terephthalic acid (polymer 18 in Table III) has a T_g of 2°C and a T-peel strength on epoxy phenolic-coated 8-mil steel of 10 lb/in. width at 0°C, whereas unmodified polyester I has a lower T_g, −10°C, and a T-peel strength of 25 lb/in. width under these conditions. Both polymers have similar melting points (ca. 164°C), and polymers with the same degree of crystallinity have similar T-peel strengths at 120°C (15–17 lb/in. width at 17% crystallinity). Increasing the crystallinity of the polymer increases its resistance to heat. The peel strength of 15 lb/in. at 120°C obtained with polyester I (17% crystallinity) was increased to 21 lb/in. when the crystallinity was 19.5%.

Ideally, then, to obtain high peel strength, a polyester should have a T_g below its lowest use temperature, a melting point appreciably above its upper use temperature, and depending upon the T_g, about 15%–20% crystallinity. The inherent viscosity should be at least 0.5 and, to control the degree of crystallinity, perhaps as high as 1.2.

Since polyester I, prepared from trans-1,4-cyclohexanedicarboxylic acid, was shown to be an excellent adhesive, other polyesters of this acid were of interest. Table III showed that there was a definite correlation of peel strength with T_g and crystallinity when polyester I was modified with various amounts of terephthalic acid or the cis/trans mixture of cyclohexanedicarboxylic acid. When the polyester I structure was changed by completely replacing the butanediol component with other diols, the polymers with the lowest crystallinity and T_g's did not have the highest peel strengths (Table IV). However, the polyesters with T_g's of 30°C or

lower had appreciable peel strengths at 23°C, and the polyesters with higher T_g's, like the polyterephthalates of Table I, had almost no peel strength at this temperature. The amorphous 1,4-cyclohexanedimethanol polyester of Table IV, however, had a peel strength of 24 lb/in. width at 70°C because at this temperature the polymer is above its T_g (52°C) and in its rubbery state.

Since our polyesters with high T_g's had low peel strengths, in view of Lee's work[9] it might be thought that these polyesters are not adequately wetting the epoxy resin-coated substrates. Lee showed that an increased critical surface tension of a polymer is associated with an increased T_g, and Zisman[10] showed that increasing the critical surface tension of an adhesive decreases its ability to wet a substrate. But although our polyesters with high T_g's did have low peel strengths, since they had high tensile shear strengths (Table I) the substrates were wetted by the molten adhesive. The low peel strengths of our higher T_g polyesters presumably are due to insufficient flexibility of the polymer chains, not to a lack of wetting.

Creep

To avoid creep in the polyester adhesive bond, the initial melting temperature should be at least 20°C above the highest test temperature. In general, the initial melting temperature observed in the DSC thermograms (departure of melting peak from specific heat curve) occurred about 20°–30° C below the melting peaks listed in Table III. If the initial melting temperature is at least 20°C above the highest use temperature, then the melting peak is at least 40°C above the use temperature. An excellent correlation was found between the initial melting temperature and the temperature for creep failure of the bond with an 80-psi load (oven heating-rate of 1.5°C/min); failure usually occurred within a few degrees of the initial melting temperature. Creep failure of polyester I under these conditions took place at 150°C.

Tensile Shear Strength

Since satisfactory peel strength over an appreciable temperature range is more difficult to attain than tensile shear strength, much of this discussion so far has been concerned with peel strength. The tensile shear strength is usually not a problem, because crystalline polyesters with high peel strengths over a given temperature range generally also have high tensile shear strengths at these temperatures. The reverse is not true, however; polyesters with high tensile shear strengths do not necessarily have high peel strengths (Table I). The tensile shear strength at elevated temperatures, as is true with peel strength, depends upon the melting point and degree of crystallinity of the polyester. But, in contrast to peel strength, improved tensile shear strength at elevated temperatures can be attained by increasing the T_g. Even if the polymer is amorphous, it can have a high tensile shear strength until its T_g is approached (Table I).

Table V shows the tensile shear strengths of a number of representative 1,4-butanediol polyesters. The first polyester, that from a *cis/trans* mixture of 1,4-cyclohexanedicarboxylic acid, is noncrystalline and has a T_g of $-11°C$. Its tensile shear strength, high at $0°C$, was greatly reduced at $23°C$ and was 0 at $70°C$. The similar polyester of the *trans*-dicarboxylic acid (example 2) has a similar T_g. However, since this polymer had an appreciable amount of crystallinity and melted at $167°C$, it had a high tensile shear strength even at $120°C$. Modification of this polyester with 20 mole-% of the *cis-/trans*-dicarboxylic acid (example 3) did not significantly affect the T_g but reduced the crystallinity somewhat and reduced the melting point appreciably. Consequently, the tensile shear strength at $120°C$ was appreciably decreased. A different modification (example 4) gave, compared with example 3, a similar crystallinity, a somewhat higher T_g, an appreciably higher melting point and, therefore, a higher tensile shear strength at $120°C$. The shear strength was not quite as high as that of the unmodified polyester of example 2, which had a similar melting point but a somewhat higher degree of crystallinity.

The adhesive bond strength of the polyterephthalate (examples 5 and 6) apparently was adversely affected by the relatively high degree of crystallinity of the polymer. The highest shear strengths were obtained with the polyester having the lower amount of crystallinity (example 6). Since a polymer shrinks in volume when it crystallizes, greater shrinkage and formation of strains occur on cooling of melt-adhesive bonds having high degrees of crystallinity.

CONCLUSIONS

The peel strength of polyesters on metals coated with epoxy resins is affected by four characteristics of the polyester: (1) inherent viscosity, (2) glass transition temperature (T_g), (3) degree of crystallinity, and (4) melting point. The inherent viscosity affects the strength, toughness, and crystallinity of the adhesive, and values of 1.0 or higher give the best results with many crystalline polyesters. The T_g affects the low-temperature properties of the adhesive, and the best performance is obtained when the T_g is below the minimum use temperature. Relatively low peel strength is obtained when the T_g is appreciably above the use temperature. The degree of crystallinity and melting point together affect the adhesive strength at elevated temperatures; insufficient crystallinity and low melting points limit the bond strength at elevated temperatures. A melting point at least $40°C$ above the maximum use temperature is desirable; high amounts of crystallinity, however, limit the peel strength by making the adhesive bonds brittle. Good peel strength can be maintained when the crystallinity is increased if the T_g is decreased. Depending upon the T_g, up to 20% crystallinity is desirable. It is important that the crystallization rate be rapid during formation of the adhesive bond and that the amount of crystallinity does not increase after the bond is formed.

Except for the T_g limitation, these factors which affect the peel strength of polyesters on epoxy resin-coated metals also are important in determining the tensile shear strength. High T_g's, however, do not limit the tensile shear strength but permit polyesters with little or no crystallinity to have high shear strength until the T_g is approached.

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