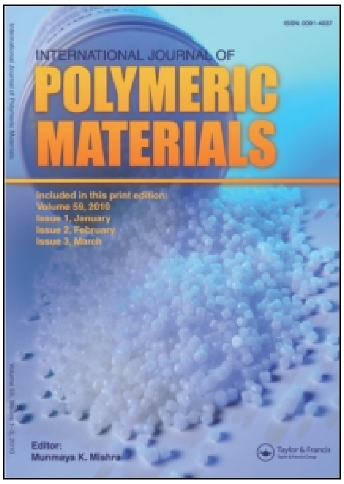

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Evaluation of Some Factors Affecting the Performance of Polyester Hot-Melt Adhesives

S. M. Aharoni[a]; D. C. Prevorsek[a]
[a] Chemical Research Center, Allied Chemical Corporation, Morristown, New Jersey

To cite this Article Aharoni, S. M. and Prevorsek, D. C.(1977) 'Evaluation of Some Factors Affecting the Performance of Polyester Hot-Melt Adhesives', International Journal of Polymeric Materials, 6: 1, 39 — 55

To link to this Article: DOI: 10.1080/00914037708075219

URL: http://dx.doi.org/10.1080/00914037708075219

Intern. J. Polymeric Mater., 1977, Vol. 6, pp. 39–55

Printed in Reading, England

Evaluation of Some Factors Affecting the Performance of Polyester Hot-Melt Adhesives

S. M. AHARONI and D. C. PREVORSEK

Chemical Research Center, Allied Chemical Corporation, Morristown New Jersey 07960

(*Received November 10, 1976*)

A study was carried out to establish the importance of rheological, thermal, and chemical variables in the performance of polyester hot-melt adhesives. The performance criteria are based on the shear strength of Al–Al lap shear joint formed under optimal conditions.

The results are presented showing the effects of: application and testing temperatures, chemical composition of the adhesive, linear *vs.* branched polymer, crystallinity, rate of crystallization and molecular weight.

INTRODUCTION

The strength of adhesive joints and structural parts joined with adhesives depends on the characteristics of adhesives, adherends and the method of the preparation of the joint. In the evaluation of adhesives it is, therefore, essential to understand the role of these variables in the properties of the joint. The present study concerns the factors affecting the strength of joints made with polyester hot-melt adhesive. The following variables are discussed:

a) Application temperature.
b) End-use temperature.
c) Chemical composition and its effect on crystallinity.
d) Chain regularity and its effect on crystallinity and crystallization rate.
e) Viscosity.

In the following, these factors are evaluated for a series of saturated polyesters employed as hot-melt adhesives.

EXPERIMENTAL

The polyesters described in this study were all prepared by a common melt-condensation procedure.[1] All bonds were between aluminum metal strips one inch wide and 0.071 inch thick. The strips were solvent-wiped and the overlap was 1 inch. Both these facts tend to reduce the psi results of the bond strength relative to the comparable ASTM test procedure D1002-64.

The mechanical testing of joints was carried out with an Instron type tester using a cross-head speed of 0.5 inch/min. The glass transition temperature (T_g), was determined using DSC technique at a heating rate of 10°C/min.

OPTIMAL APPLICATION TEMPERATURE

The optimal application temperature of a hot-melt adhesive is the temperature range at which all the following criteria coexist:

a) The polymer is in the molten state possessing relatively low melt viscosity.
b) The polymer wets the substrate and the failure of bonds is cohesive and not adhesive in nature.
c) The fluidity of the polymer is not excessive, so that the polymer is not ejected from the bond area under the bonding pressure.
d) Hydrolytic and thermal degradation are not yet significant.

In crystallizable polyester, these conditions limit the optimal temperature range to that from T_m to less than the decomposition temperature T_{dec}. Plots of bond strength *vs.* temperature in Figures 1 and 2, bear out this assertion. Here the mechanical testing was performed at room temperature (R.T.) but it was established that the poorer results, obtained from samples bonded at temperatures other than the optimal application temperature, are independent of the temperature of testing.

Correlations of plots of bond strength *vs.* temperature of application with DTA scans of partially crystalline polyesters reveal that, generally, bond strengths increase from zero at T_m to a maximum value at about $T_m + 80°C$ and then drops precipitously to reach negligible values at $T_m + 150°C$. For a highly crystalline polyester, such as PET, the range of change in bond strength is narrower: zero strength at T_m, maximum at $T_m + 55°C$ and dropping to about zero again at $T_m + 100°C$.

OPTIMAL END-USE TEMPERATURE

Plots of bond-strength *vs.* temperature of testing, Figures 3 through 6, indicate that the highest bond strength is obtained at the glass transition temperature,

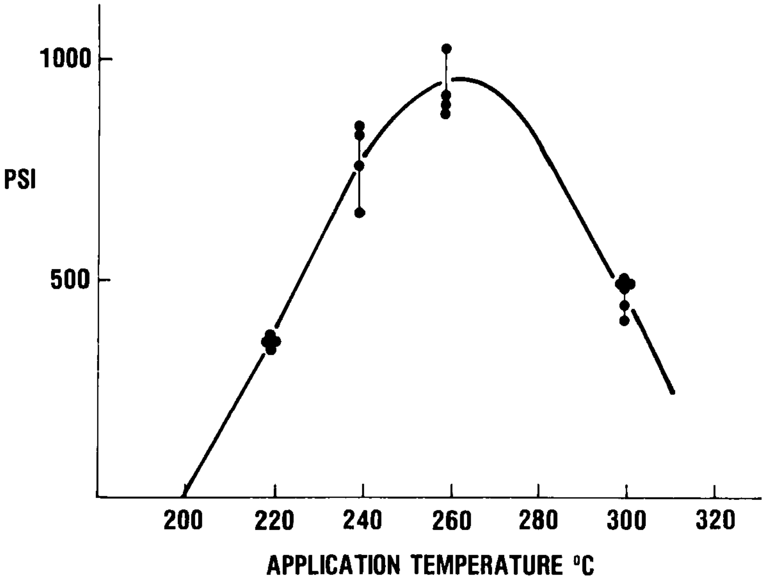

FIGURE 1 Aluminum-aluminum lap shear joint tested at room temperature. Effect of *application* temperature. Polyester of (80 terephthalate + 20 isophthalate)/1,4-butanediol. Melting temperature (T_m) = 200°C, $T_{\text{appl.}} = T_m + 60°C$ = optimal application temperature.

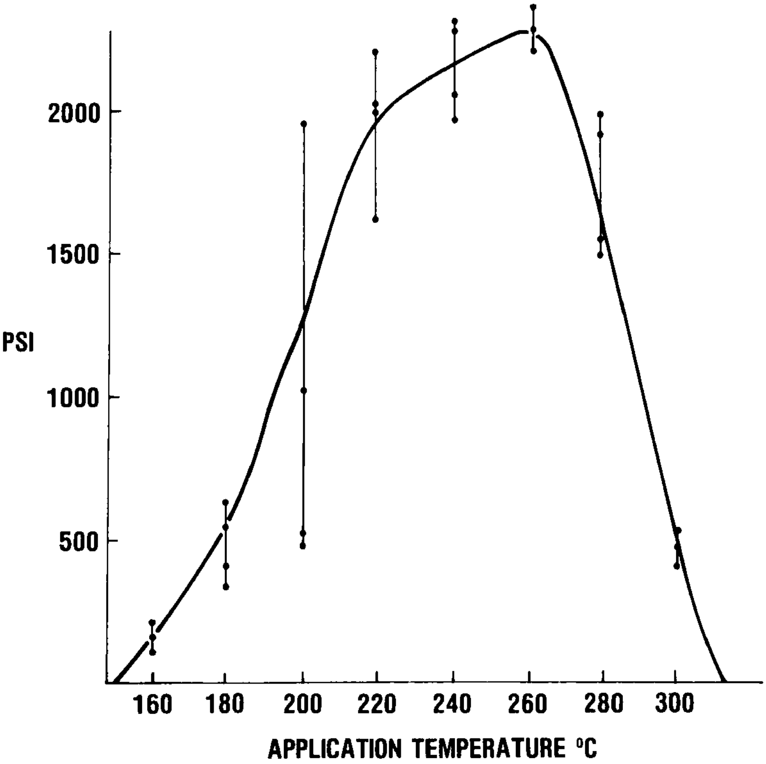

FIGURE 2 Aluminum-aluminum lap shear joint tested at room temperature. Effect of *application* temperature. Polyester of (60 terephthalate + 40 isophthalate)/1,4-butanediol. Melting temperature (T_m) = 156°C, $T_{\text{appl.}} = T_m + 70°C$.

T_g, of the polymer.[2] The bond strength drops sharply above T_g, especially for amorphous polymers, as the polymer becomes more fluid and loses its load-carrying capability. Below T_g the bond strength drops also, although not as sharply as above T_g, because of the increased rigidity and brittleness of the polymer. At T_g, where there is a sharp drop in strength (Figure 6), there exists a combination of chain mobility that imparts sufficient cohesiveness to the bulk to carry heavy loads and yet allows for the greatest energy dissipation

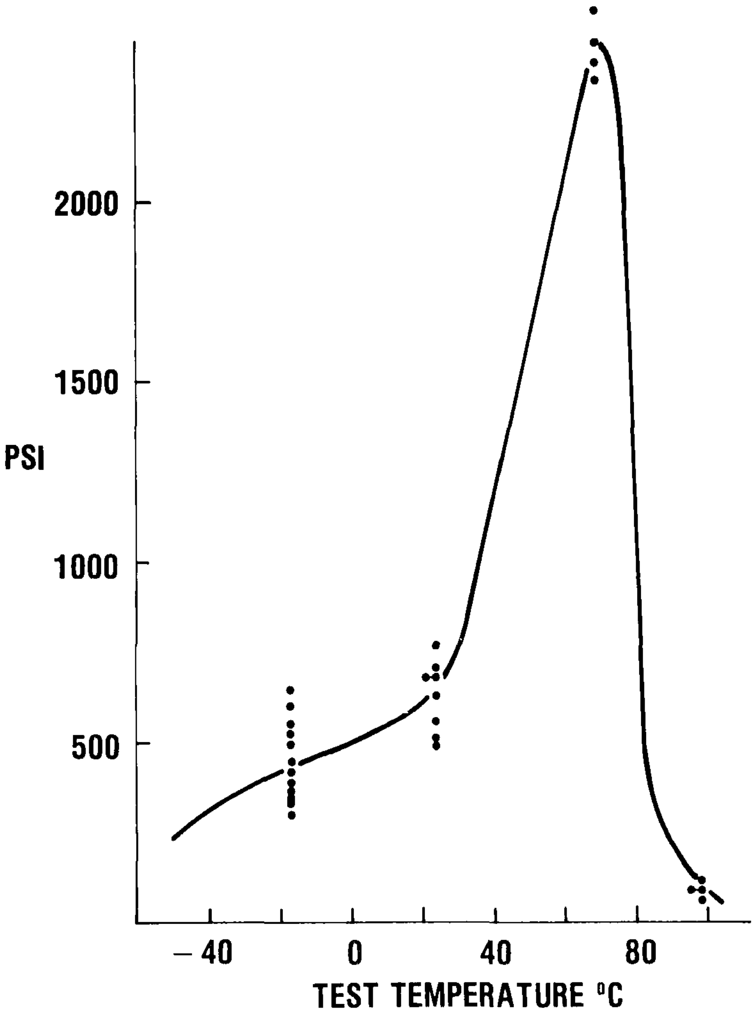

FIGURE 3 Aluminum–aluminum lap shear joint tested at different temperatures. Optimum *performance* temperature. Polymer of (60 terephthalate + 40 isophthalate)/ethylene glycol. T_g = 68°C.

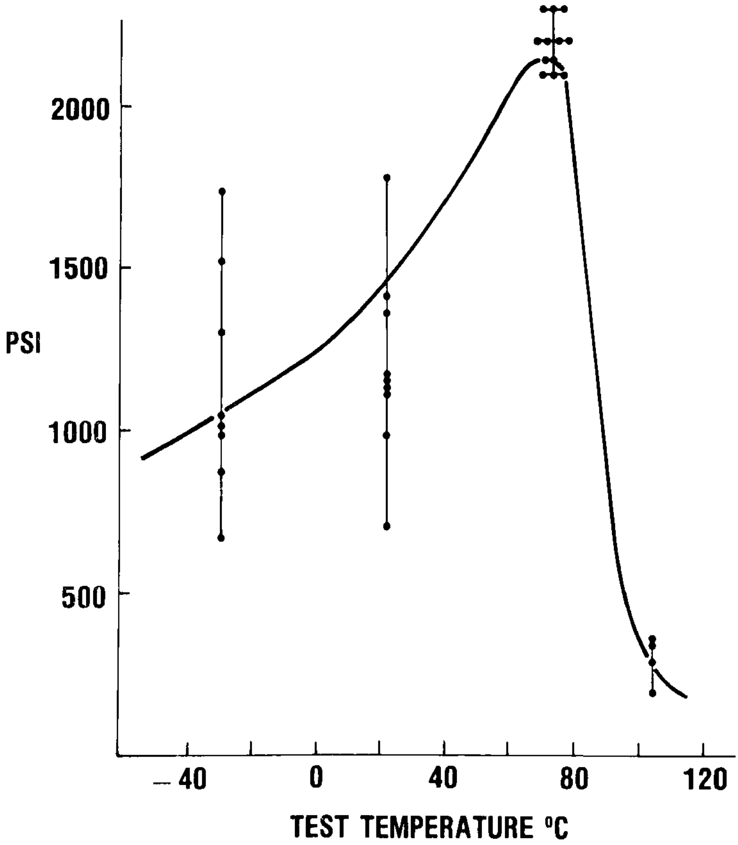

FIGURE 4 Aluminum-aluminum lap shear joint tested at different temperatures Optimum *performance* temperature. Polymer of (80 terephthalate + 20 isophthalate)/ethylene glycol. $T_g = 74°C$.

through chain motion.[3] This is evident from the large mechanical loss peak close to T_g, Figure 7; that is, at T_g a large fraction of the energy imparted to the polymer is dissipated within it. While the position of a loss peak is clearly correlated with the optimum bond strength of each polymer, at the temperature interval close to T_g, it is interesting to note that when different polymers are compared on a quantitative level such a correlation has not been found between their loss peak intensity and their bond strength. This is apparent from Table I. The reasons for this lack of correlation are not yet fully understood.

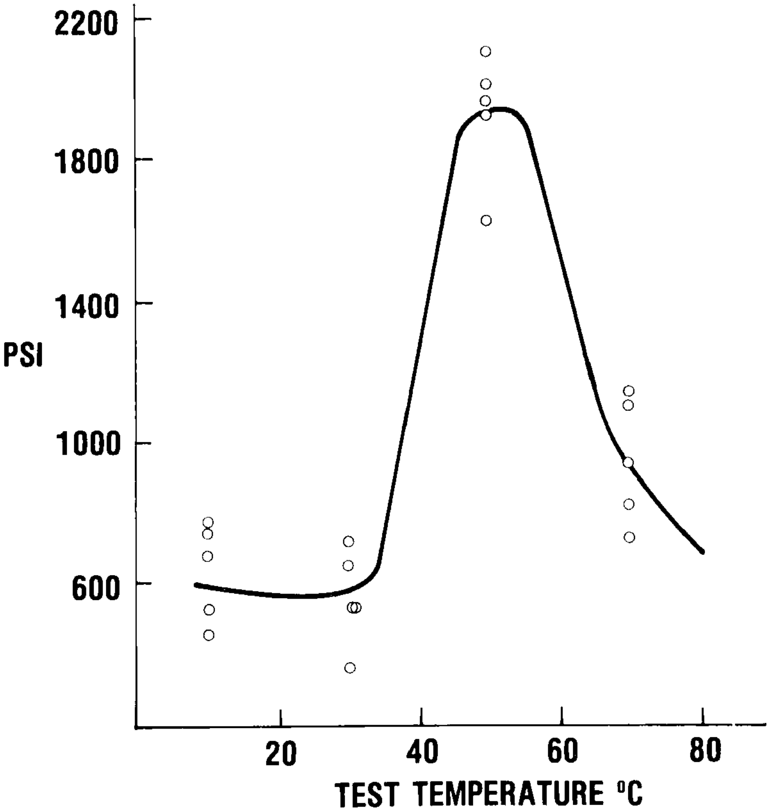

FIGURE 5 Aluminum-aluminum lap shear joint tested at different temperatures. Optimum *performance* temperature. Polymer of (64 terephthalate + 16 sulfone bis(4-phenyl carboxylate) + 20 adipate)/ethylene glycol. $T_g = \sim 50°C$.

EFFECTS OF CHEMICAL COMPOSITION ON *Tg* AND ON END-USE TEMPERATURE

The character of the diacids in a polyester affects the T_g of the resultant material and, therefore, its optimal end-use temperature. This is obvious from Table II. Table III relates to copolyesters of terephthalic and isophthalic acids with ethylene glycol. Here the changes in T_g with composition are much smaller. Another example, in Table IV, are the copolyesters of terephthalic and adipic acids. Changes in the diol composition also cause shifts in the T_g and end-use temperature of the copolyesters. Table V indicates that copolyesters of terephthalic and adipic acids with ethylene glycol or with 1,4-butanediol show significant changes in T_g. The T_g may not change, or change very little, as a

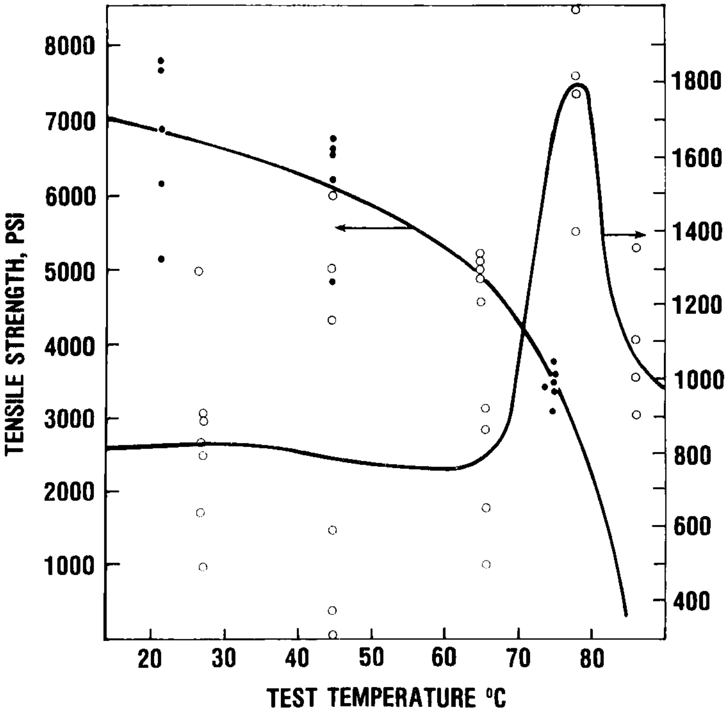

FIGURE 6 Effect of temperature on the tensile strength of the adhesive and on the strength of Al–Al lap shear joint prepared from the same adhesive.
● Tensile strength; ○ Lap shear strength.

result of the replacement of one diol by another if their flexibility is about the same. This is evident from the data in Table VI. In the case of a high T_g polyester prepared from bisphenol-A and phthaloyl chloride there is no change in T_g when terephthalic acid replaces isophthalic acid (Table VII). When a rigid diol was introduced instead of bisphenol-A the T_g increased and when a very flexible diol replaced bisphenol-A the T_g dropped sharply (Table VIII).

Finally, it is known that T_g is affected by the molecular weight of the polymer. At low molecular weights the change of T_g is very strongly dependent on the molecular weight but this dependence changes over a relatively narrow range and tapers to a very mild dependence of T_g on molecular weight.[4-6] Terephthalate/isophthalate copolyesters were polymerized for varying periods under otherwise similar conditions and the first heat-up in the DSC shows, in Table IX, a neat correlation between the viscosity and the T_g. Since, unlike PET, the relationship between the $[\eta]$ and molecular weight of the copolyesters is not known, one can only notice trends but not draw quantitative conclusions.

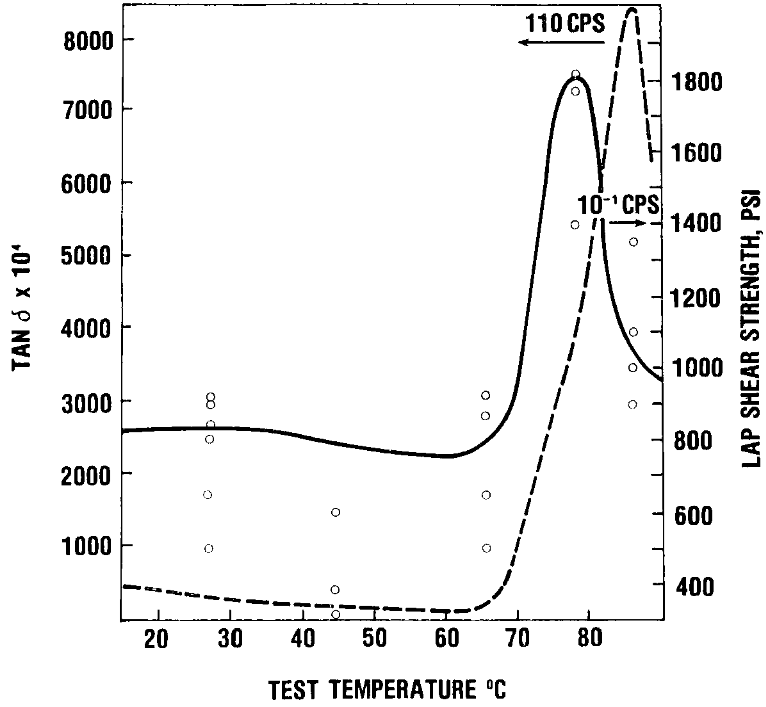

FIGURE 7 Effect of temperature on the mechanical loss and on the strength of adhesive joints prepared from the same adhesive. (In testing of joints, the failure occurred in about 10 seconds. Therefore, the frequency of strength experiment is about 10^{-1} cps. The mechanical loss was measured at 110 cps. The application of the time-temperature correspondence principle will reduce the difference in the position of the peaks.)

TABLE I

Tan δ peak and maximum joint strength

Polyester	T_g °C (10^{-1} cps)	T_{tan} (110 cps)	Tan δ	Maximum joint strength at T_g
Linear PET	75	103	0.90	1800 lb
Branched PET	63	84	0.86	2700 lb
80:20 tere/adipic + E.G.	22	41	1.43	2400 lb
64:16:20 tere/sulfone/adipic	34	56	1.2	2000 lb

EFFECTS OF BRANCHING

It was hypothesized that branched molecules will be less prone to fast and extensive crystallization and, hence, yield hot-melt adhesives with higher bond

TABLE II

Effect of diacid on T_g

Acid	%	Diol	%	T_g °C
2,6-naphthalene dicarboxylic	100	ethylene glycol	100	120
terephthalic	100	E.G.	100	75

TABLE III

Effects of terephthalic/isophthalic acid ratio

Terephthalic acid	Isophthalic acid	T_g, C
100	0	75
80	20	67
60	40	63
40	60	61
20	80	58
0	100	61

TABLE IV

Effects of terephthalic/adipic acid ratio

Terephthalic acid	Adipic acid	T_g, C
100	0	75
80	20	39
70	30	23
60	40	10

TABLE V

Effects of diol on T_g

Terephthalic acid	Adipic acid	Ethylene glycol	1,4-butanediol	T_g, °C
60	40	100	0	10
60	40	0	100	34

strength than the corresponding fully linear polymers. Therefore, a program aimed at proving or disproving this hypothesis was undertaken.

Several polyesters were prepared by melt polymerization, each containing predetermined amounts of glycerol in the chain as a branching agent. The molar amounts of glycerol were varied as follows: 0%, 0.17%, 0.34%, 0.51% and in one instance 0.68%. The polymers used for evaluation were: PET, 80/20 terephthalate/adipate copolyester with ethylene glycol, and 60/40 terephthalate/adipate copolyester with ethylene glycol.

TABLE VI

Effects of ratio of diols on T_g

Diol 1	%	Diol 2	%	Diacid	%	T_g, °C
Ethylene glycol	100	bisphenol-A bis-(β-hydroxyethyl) ether	0	Terephthalic acid	100	75
E.G.	70	bisphenol-A bis-(β-hydroxyethyl) ether	30	Terephthalic acid	100	80
E.G.	30	bisphenol-A bis-(β-hydroxyethyl) ether	70	Terephthalic acid	100	81
E.G.	0	bisphenol-A bis-(β-hydroxyethyl) ether	100	Terephthalic acid	100	78
E.G.	50	bisphenol-A bis-(β-hydroxyethyl) ether	50	Terephthalic isophthalic	60 40	72

TABLE VII

Effects of acid isomerism on T_g

Diacid	%	Diol	%	T_g,°C
Terephthalic acid	100	Bisphenol-A	100	150
Isophthalic acid	100	Bisphenol-A	100	153

TABLE VIII

Effects of aromatic diols on T_g

Diol	%	Diacid	%	T_g, °C
Hydroquinone	100	Isophthalic acid	100	173
1,5-Naphthalene diol	100	Isophthalic acid	100	173
Bisphenol-A	100	Isophthalic acid	100	153
Resorcinol di-(β-hydroxyethyl) ether	100	Isophthalic acid	100	58

TABLE IX

Viscosities of similar copolyesters

Composition	[η]	T_g, °C
80/20-terephthalate/isophthalate + ethylene glycol	0.70	74
80/20-terephthalate/isophthalate + ethylene glycol	0.53	67
60/40-terephthalate/isophthalate + ethylene glycol	0.56	68
60/40-terephthalate/isophthalate + ethylene glycol	0.51	63

In the case of PET it was found that the improvement in bond strengths upon branching was a marginal improvement of a few hundred psi at the most. PET shows a very large scatter of the bond strength data points, evidently reflecting the coexistence of ductile and brittle failure mechanisms, and the small changes in bond strength, albeit existing, were smaller than the data scatter.

In the terephthalic/adipic acid copolyesters it was found that if the fully linear copolymer exhibited good bond strength, as the 80/20 polymer did, then the addition of chain branches did not increase appreciatively the bond strength. If the fully linear copolymer exhibited poor bond strength, as the 60/40 polymer did, then the branching did improve its performance remarkably. This remarkable improvement, however, brought the polymer only to the level of performance of the fully linear PET and not above it. It should be noted that the 80/20 and 60/40 copolyesters data show much smaller scatter than the linear or branched PET.

Following the rate of isothermal crystallization of linear and branched PET by means of densitometry measurements, revealed that the initial and final densities of the completely amorphous and fully crystalline polymers were the same. The crystallization of the branched PET lagged behind that of the linear PET, indicating a longer initial incubation period but showed essentially the same rate of density change (crystallization) once crystallization became significant. Figure 8 is a graphic description. It may be that these variations in crystallization and the consequential changes in melt viscosity are significant contributors to the variations in adhesion characteristics observed upon branching the linear polyesters.

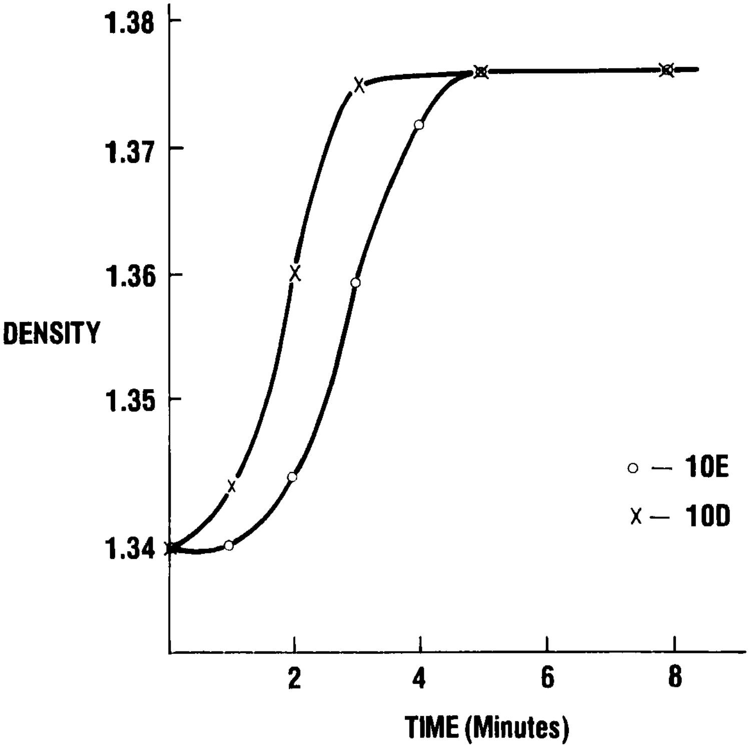

FIGURE 8 Effect of branching of PET on rate of crystallization. Material 10D is linea PET with intrinsic viscosity of 0.65. Material 10E is branched PET with intrinsic viscosity of 0.62.

It is worthwhile to note here that when 0.51 % mole branching agent was used the gelation of PET could be effected simply by increasing the duration of the second step in the melt polymerization from one to two hours.

According to Flory[7] at the gel point

$$(\bar{Y}_w - 1) = 1/\rho$$

where $\bar{Y}_w$ = weight average degree of polymerization and ρ is the ratio of branch-forming ends to total end groups. For 0.51 % mole trifunctional groups

$$\rho = \frac{0.0051 \times 3}{1.00 \times 2 + 0.0051 \times 3} = \frac{0.0153}{2.0153} = 0.00759, \ 1/\rho = 132$$

and $\bar{Y}_w$ = 133 corresponding to a molecular weight of about 26000 with I.V. of about 0.40. After one hour of run the reaction usually yielded higher I.V.'s but no gelation, indicating that the gelation was not as efficient as expected from theory and that a higher DP is probably required to effect the gelation.

ROLE OF CRYSTALLINITY AND CRYSTALLIZATION RATE

The crystallizability of polymers seems to be associated with the ability of the polymer chains to pack in register both laterally and longitudinally. This calls for a high degree of regularity along the chain, avoiding excessive branching, twisting, folding and irregularly positioned pendant groups that will destroy the regularity along the chain and obstruct lateral packing.

The rate of crystallization depends also on such kinetic parameters as the rate of cooling and the absolute temperature interval below the melting temperature.

In the course of this work it was found that polymers which are highly crystalline and whose rate of crystallization is high, yield rather poor adhesive joints. When such polymers are employed as hot-melt adhesives, the joint fails usually at the polymer-to-substrate interface and the polymer delaminates from the substrate. It is believed that when highly crystalline polymer with a high rate of crystallization cools from the melt, a large scale material reorganization takes place. This is associated also with a sharp reduction in volume since the material contracts by about 10% upon going from the amorphous to the crystalline state.[8] The material shrinkage generates a large number of internal voids in the polymer. It also pulls the polymer off the substrate. The large scale fast molecular reorganization leaves the frozen polymer with a high level of residual internal stresses. It is also possible that the high amount of crystallinity leaves the polymer surface with only a small fraction that can conform to the surface of the substrate and form a reasonable bond. Hence, it can be concluded that with fast crystallizable polymers the following effects prevent the formation of a strong adhesive joint; (a) excessive volume contraction and voiding, (b) high residual stresses, and (c) deficient wetting of the substrate.

Therefore, a good hot-melt adhesive must not possess an excessive amount of crystallinity and the rate of crystallization of the material must be kept low.

The solution of this problem can be achieved from, at least, two approaches. In the first, chemical changes are introduced into the polymer but the chains are kept linear throughout. Here, for example, the isophthalic residue can replace, in part or in total, the terephthalic residue, forcing a bend or a twist in the molecule. Another modification is an irregular change in length or bulkiness of one of the monomers. The replacement of ethylene glycol by bisphenol-A bis(β-hydroxyethyl) ether is an example to such a modification. The second approach introduces physical obstacles to high crystallinity and, especially, high rate of crystallization, such as chain branches and crosslinks. This can be easily achieved in polyesters by the careful addition of tri- or tetra-functional groups during the polymerization reaction, or by the addition of small amounts of crosslinking agents to fully polymerized crosslinkable polymers.

EFFECTS OF INTRINSIC VISCOSITY ON BOND STRENGTH

The intrinsic viscosity (I.V.) of hot-melt adhesives significantly affects their bond strengths. When the I.V. of polymers is low, say below 0.4, the resultant polymer is rather brittle and the adhesive bond strength is extremely low. If the I.V. of the polymer is rather high, say 0.9 and above, the molten polymer flows very poorly and does not wet the substrates well. This results in poor bonds that fail in an adhesive manner. The range of I.V. suitable for hot-melt polyester adhesives is, therefore, 0.4 to 0.85, and its peak performance is at about $[\eta] = 0.7$. The minimum application temperature required to achieve good bonding and the optimum application temperature both increase with increasing molecular weight of the polymer. This is indicated in Figures 9, 10, and 11. It may be claimed that a reduction in % crystallinity, due to higher viscosities, is responsible for the improved performance. The data in Figure 11, for a fully amorphous polymer, belie this contention. Note also the difference in scatter in the results of Figures 9 and 10, where testing is carried out at 23°C, and the low temperature data of Figure 11. The observed increase in scatter with decreasing temperature of testing is a result of the embrittlement of the adhesive layer and higher concentration of stress at discontinuities in the joint.

CONCLUSIONS

In comparing the properties (tan δ, strength, etc.) of an adhesive layer with the properties of the adhesive joint it must be remembered that the mode of failure and application of stress in an adhesive specimen and adhesive joint are different. Adhesive joint is a composite structure where the adhesive layer usually exhibit large residual stresses, and the mode of deformation is shear. A sample

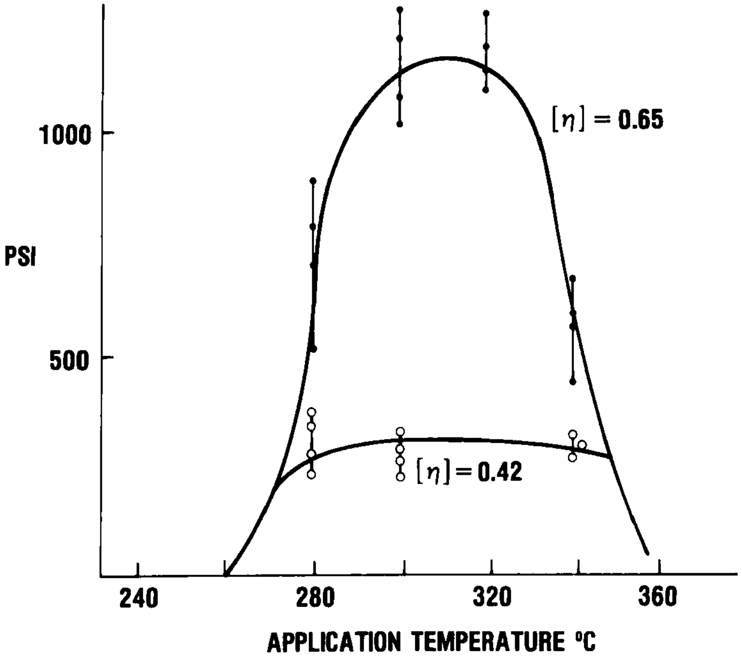

FIGURE 9 Effects of application temperature and polymer viscosity on Al–Al lap shear joint strength at room temperature. Polymer: PET.

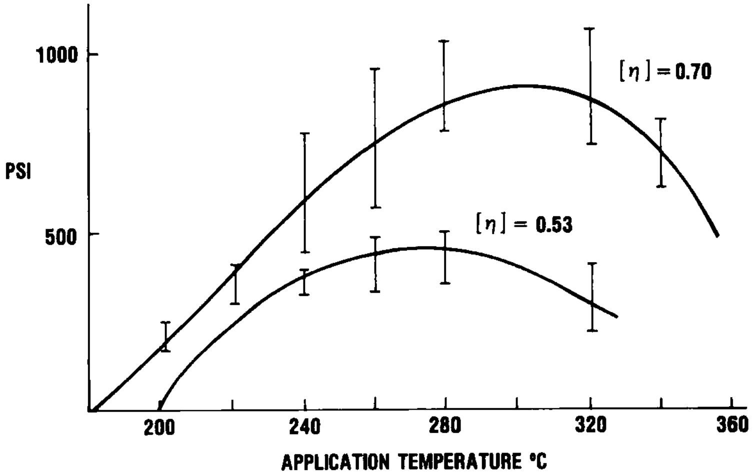

FIGURE 10 Effects of application temperature and polymer viscosity on Al–Al lap shear joint strength at room temperature. Polymer: (80 terephthalate + 20 isophthalate)/ethylene glycol.

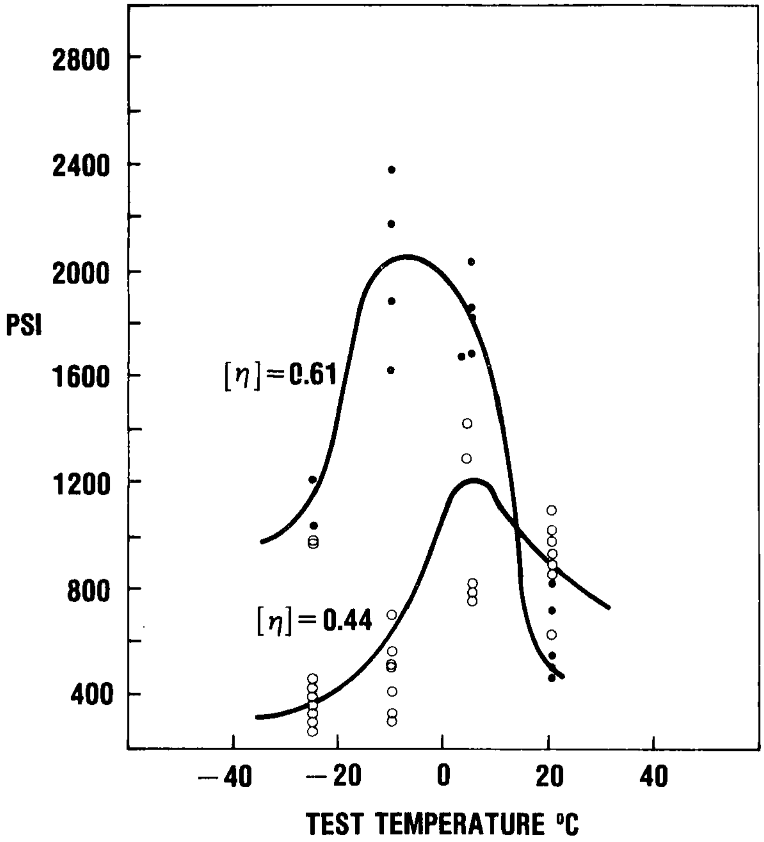

FIGURE 11 Effects of polymer viscosity on Al–Al lap shear joint strength at various emperatures. The polymer was the amorphous (60 terephthalate + 40 adipate)/ethylene glycol.

of polymeric adhesive is, on the other hand, frequently tested in tension and the specimens may have quite different thermal and stress history.

Therefore, it is impossible to design experiments which would allow the prediction of strength of an adhesive joint on the basis of measurements conducted on specimens prepared solely from adhesives. Nevertheless, this study showed that for the properties of adhesive joints prepared with hot-melt adhesives several useful correlations can be derived on the basis of measurements carried out with the polymeric adhesives.

1) Optimum application temperature is about $T_m + 60°C$.

2) Optimum end-use temperature is at T_g of adhesive.

3) Brittle and low molecular weight polyesters do not give good adhesive bonds. But adhesive joint strength does not correlate with polymer strength.

4) Fast crystallizing polymers are not suitable for hot-melt adhesives.

5) In poor performing (e.g. fast crystallizing) polyesters, branching improves adhesive strength.

6) A minimal molecular weight (M_n) of about 15,000 is required to achieve good adhesive strength with polyester.

7) All polyesters which meet criteria of M_n, toughness, low rate of crystallization, and can be applied without significant degradation-yield at T_g a lap shear strength of ~2500 psi.

8) Temperature of maximum adhesive joint strength correlates with temperature of tan δ peak.

9) Adhesive joint strength does not correlate with tan δ amplitude or tan δ area.

10) At optimum end use temperature (i.e., at T_g of adhesive) the adhesive joints are not suitable for applications where the assemblies are exposed to prolonged exposure to stress because of creep.

Finally, it must be pointed out that the conclusions derived above are qualitatively applicable to other types of joints such as butt joints, etc. This conclusion is supported by several experiments which are not reported in this article.

References

1. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Second Edition (Interscience, New York, 1968), p. 130ff.
2. D. H. Kaelble, *Physical Chemistry of Adhesion* (Wiley-Interscience, New York, 1971), pp. 455–456.
3. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids* (Wiley, London, 1967), p. 43ff.
4. P. J. Flory and T. G. Fox, *J. Polymer Sci.* **3**, 647 (1948).
5. B. Ke, *Polymer Letters* **1**, 167 (1963).
6. J. J. Keavney and E. C. Eberlin, *J. Appl. Polymer Sci.* **3**, 47 (1960).
7. P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, N.Y., 1953), pp. 348–361.
8. D. W. van Krevelen, *Properties of Polymers* (Elsevier, Amsterdam, 1972).