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Principles of the Adhesion of High Polymers

Part 1 *Factors Affecting the Bonding of Poly(ethylene terephthalate) Film*

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The influence of various factors on the bonding of poly(ethylene terephthalate) film is discussed. These factors include surface energy, weak boundary layers, and the mechanical properties of the adhesive. Data are presented in an attempt to demonstrate the relative importance of these various factors. In order to study the effect of the mechanical properties of the adhesive on the resultant bond strength, a series of thermoplastic polyesters has been prepared. This has enabled a variation in mechanical properties to be made with a minimum change in other properties.

1. Introduction

It is generally recognised that many factors can affect the strength of an adhesive joint [1]. However, in many cases, particularly where polymeric substrates are involved, the relative importance of these factors is usually unknown. This means that, when bonding problems are encountered, their solution is obscure and, in the past, empirical approaches have had to be used to solve these problems. However, the increasing amount of work on more fundamental aspects of adhesive bonding that is taking place in many laboratories throughout the world should lead to more rapid and effective solutions to these problems.

A number of theories of adhesion has been proposed including the adsorption, diffusion, and electrostatic theories and these, in particular the adsorption and diffusion theories, have been the subject of much discussion [2-5]. In the authors' view, diffusion is likely to be comparatively rare, and the adsorption theory is adopted in this paper.

It is clear that bonding and testing conditions (e.g. strain rate) have an effect on the strength of an adhesive joint, but these cannot be regarded as basic reasons for bonding problems. A number of basic reasons for bonding problems have been proposed. Zisman [6] has suggested that bonding problems associated with non-polar polymers are largely due to insufficient contact between the adhesive and the substrate, and he has discussed in detail how the relative surface energies affect the degree of contact. However, Bikermann [7] and Hansen and Schonhorn [8] have provided evidence to show that regions of low strength at the interface of an adhesive joint (weak boundary layers) can have a catastrophic effect on the bond strengths obtained involving polymeric substrates such as polyethylene and polytetrafluoroethylene. Weak boundary layers are by no means limited to polymeric substrates. For example, Bullett and Prosser [9] point out that the poor adhesion of paints to various metals can be explained in terms of weak boundary layers arising from a number of sources, for example owing to the reaction products between the paint and metal surfaces.

The viscosity and the mechanical properties of the adhesive are also important considerations. It is clear that the viscosity of the adhesive at the time of application must be sufficiently low to enable it to penetrate at least the gross irregularities of a surface. The mechanical properties of the adhesive after solidification must be appropriate to the type and magnitude of the forces to which it will be subjected in practice.

Bonding problems involving poly(ethylene terephthalate) film are encountered fairly frequently and no satisfactory explanation for this has been given. The object of this paper is to attempt to clarify the factors that are most important in the bonding of poly(ethylene terephthalate) film. In particular, the importance of surface energies, of weak boundary layers, and of mechanical properties is discussed. In order to study the effect of the mechanical properties of the adhesive on the resultant bond strength, a range of thermoplastic polyesters based on caprolactone, ethylene terephthalate, and ethylene isophthalate has been prepared. This has enabled a variation in the mechanical properties to be made with a minimum change in chemical and other properties, which would otherwise complicate the interpretation of the results. Only one grade of polyester film has been examined (see section 2.1), but it is felt that the general conclusions reached will be applicable to most other types.

This paper is the first part of a series on the bonding of various polymeric substrates.

2. Experimental

2.1. Materials Used

Araldite AV 100 is an epoxy resin sold by Ciba (ARL) Ltd* and Araldite HV 100 is the appropriate curing agent which is used in the ratio 1:1. Araldite AY 18 and Araldite HZ 18 are another epoxy resin system marketed by Ciba Ltd. Elvax 260 is an ethylene-vinyl acetate copolymer sold by E. I. Du Pont de Nemours & Co†. Flexalyn 80 M and Staybelite Ester 10 are rosin esters sold by Hercules Powder Co Ltd‡. Eastman 910 is a cyanoacrylate made by Tennessee Eastman Co§.

The poly(ethylene terephthalate) film used was Melinex, grade "O", 500 gauge film. Alkathene WJG 11 is a low-density polyethylene with a melt flow index of 2. These two materials are products of the Imperial Chemical Industries Ltd.

The caprolactone polyesters (BEH 2-6) were prepared by co-condensation of ϵ-caprolactone, ethylene glycol, and dimethyl terephthalate, and in some cases also with dimethyl isophthalate. BEH 1 is a high-molecular-weight polyesteramide prepared by co-condensing ϵ-caprolactone with hexamethylene diammonium adipate.

2.2. Contact-Angle Measurements

The Melinex film was first carefully cleaned with ethanol and then dried in a vacuum oven at 60° C for 30 min. A small amount of the adhesive (0.02 cm^3) was carefully placed on the Melinex film which itself was placed in an air-cell with plain glass walls. The air-cell was placed in an oil-bath whose temperature was controlled to $\pm 0.1°$ C, and nitrogen was passed through the apparatus to reduce any oxidation of the adhesive or the polyester film. When the required temperature had been reached, contact angles were measured by means of a telescope-goniometer [10], the linear magnification being about 25.

Owing to the high viscosities of the Elvax 260 blends and Araldite AV 100, it is unlikely that equilibrium had been reached in these cases and the true contact angles would probably be lower than those quoted in table I. The values quoted in table I are the mean of at least five determinations.

2.3. Butt Joints

Discs of Melinex film (1 in. diameter) were bonded to aluminium rods (1 in. diameter) with Araldite AV 100. Two such Melinex discs were then bonded together (fig. 1) with Araldite AV 100, mixed with Araldite HV 100, at 100° C for 30 min at 5 lb/in.^{2}, a glue-line thickness of 0.005 in. being maintained by means of wire spacers (1.0 in. = 2.5 cm; 1 lb/in.^{2} = 7×10^{-2} kg/cm^2).

The adhesive joints were placed in a constant-humidity cabinet (25° C, 43% relative humidity) for 24 h. The bond strengths of these joints were then determined at 25° C using a Hounsfield tensometer (type W) at a withdrawal rate of 0.25 in./min. The bond strengths quoted in table II are the mean of at least ten determinations. These experiments were repeated using Melinex film which had been extracted with trichloroethylene (at boiling point) for 80 h and subsequently dried in a vacuum oven at 70° C for 30 min. For comparison, the polyester film was replaced by a film (0.020 in. thick) of Alkathene WJG 11 which had been treated with chromic acid on the side bonded to the aluminium; in this case, the adhesive was cured at

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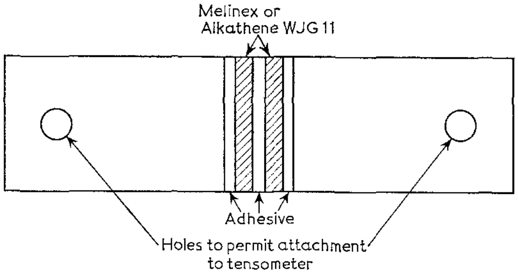

Figure 1 Butt joint (not to scale).

60° C for 3 h, rather than at 100° C, to prevent the polyethylene from melting onto the cured epoxy resin [11]. In all these cases, failure occurred between the two films and not between the aluminium and a film.

Butt joints were also formed between two rods of aluminium which had been treated with chromic acid [11].

2.4. Shear Tests

Laminates similar to those described by Sharpe and Schonhorn [11] were used, except that double lap joints were used. The curing conditions and testing procedure were identical to those employed in the butt-joint studies.

2.5. Peel Tests

In the cases of thermoplastic adhesives (i.e. caprolactone polymers and Elvax 260), an amount of adhesive calculated to give 0.005 in. glue-line thickness was placed between two sheets of the polyester film, which were then placed in a heated press, the glue-line thickness being maintained by means of shims. A pressure of 100 lb/in.^{2} at the appropriate temperature (optimised in each case) was maintained for 10 min. Unless otherwise stated, the bonded sheets were then removed from the press and allowed to cool under the slight pressure produced by a cold backing plate. This process clearly produces rapid cooling.

In the case of Araldite AV 100, this was mixed thoroughly with an equal volume of Araldite HV 100 and then cured between two sheets of the polyester film at 100° C for 30 min at a pressure of 5 lb/in^2.

The bonded sheets were placed in a constant-humidity cabinet (25° C, 43% relative humidity) for 24 h prior to testing. The bond strengths (T-peel test) of 1 × 9 in. strips were determined using a Davenport tensometer equipped with an oven, at a withdrawal rate of 4.5 in./min. The testing temperature was 25° C unless otherwise stated. The peel strengths recorded in tables IV-VII are the mean of ten determinations.

2.6. Blending

The blending of the Elvax 260 with the rosin esters was carried out in glass tubes (12 in. long, $2\frac{1}{4}$ in. diameter) fitted with a helical stirrer, the tubes being immersed in a silicone oil-bath at 160° C. The stirring rate was gradually increased to 40 rev/min and maintained at this speed for 20 min.

2.7. Mechanical Properties

The tensile properties of the polymers were determined on a Hounsfield tensometer (type E) at a strain rate of 200%/min. The polymers were conditioned in the same way as the adhesive joints; for example, the measurements were usually carried out 24 h after moulding.

2.8. X-ray Measurements

The percentage crystallinity of the polymers was determined with a Philips X-ray diffractometer at a scanning speed of $\frac{1}{2}°2\theta$/min, where 2θ is the angle between the diffracted and incident beams. Divergence and scatter slits of 1° were used. The degree of crystallinity was estimated by comparing the area under the sharp diffraction peaks with the total area under the diffraction scan.

3. Results

See tables I-VIII.

4. Discussion

4.1. Degree of Contact

It is generally considered that the degree of intermolecular contact between the adhesive and the substrate will normally have an important effect on the resultant bond strength. Increasing the intermolecular contact not only increases the area of bonding, but it also reduces stress concentrations due to voids [12]. The degree of contact will depend on the surface energies of the adhesive and the substrate [6], and also on the viscosity of the adhesive [13]. However, it is not known what degree of contact is necessary to achieve the required bond strength or in fact to exceed the cohesive strength of one of the materials which constitute the adhesive joint.

Contact angles are regarded as a useful inverse measure of the degree of contact from the surface energy viewpoint. Zisman and coworkers [14-16] have determined the contact angles between many pure liquids and smooth low-energy substrates including many polymers. They found that a relationship exists between the cosine of the contact angle and the surface tension for each homologous series of organic liquids. This led Zisman to propose his idea of critical surface tension of wetting, γ_c, which is the intercept of the line $\cos\,\theta = 1$ with the extrapolated straight-line plot of $\cos\,\theta$ against surface tension (fig. 2). The surface energy of poly(ethylene terephthalate) is high compared with most other polymers ($\gamma_c \simeq 43$ dyn/cm) [6] and, on this basis, difficulties in bonding polyester film are not expected. This is confirmed by the results in table I, which shows that a range of adhesives form low contact angles with Melinex film.

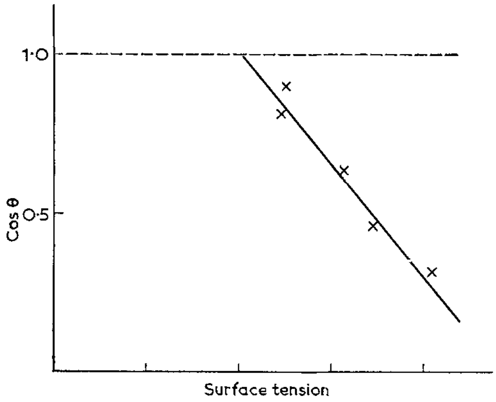

Figure 2 Critical surface tension.

Increased contact can clearly be achieved by lowering the viscosity of an adhesive. However, a number of the adhesives examined in this study, although unsuitable for bonding polyester film, are known to be effective for bonding a variety of other substrates. If viscosity was the basic reason for the bonding problems associated with polyester film, it would imply that polyester film has a unique surface geometry which considerably reduces the degree of contact with the adhesive. The bond strengths quoted in tables II and III confirm that a substantial degree of contact is achieved with a standard epoxy resin.

TABLE II Strength of butt joints formed with Araldite AV 100.

Adherends	Mean bond strength (kg/cm^2)	Type of failure
Melinex/Melinex	130	Apparent adhesive failure*
Extracted Melinex/ extracted Melinex	160	,,
Aluminium/aluminium	185	,,
Alkathene WJG 11/ Alkathene WJG 11	8.5	,,

*see section 2

TABLE III Strengths of lap joints formed with Araldite AV 100.

Adherends	Mean bond strength (kg/cm^2)	Type of failure
Melinex/Melinex	115	Apparent adhesive failure
Extracted Melinex/ extracted Melinex	130	,,
Aluminium/aluminium	260	,,
Alkathene WJG 11/ Alkathene WJG 11	9	,,
Melinex/Melinex*	62	,,

*BEH 1 used instead of Araldite AV 100

TABLE I Contact angles between various adhesives and Melinex film.

Adhesive		Temperature (° C)	Time before contact angle measured	Contact angle
Elvax 260 Flexalyn 80 M	1 3	120	60 min	12°
Elvax 260 Flexalyn 80 M Staybelite Ester 10	1 1 3	120	50 min	10°
Araldite AV 100 Araldite HV 100	1 1	100	10 min	13°
Araldite AY 18 Araldite HZ 18	4 3	80	5 min	Spreads
Eastman 910		25	5 sec	Spreads

4.2. Weak Boundary Layers

If a weak layer exists within an adhesive joint, the breaking stress of that joint will be low, however good the contact. It is becoming increasingly recognised that weak boundary layers play an important part in the bonding of many polymers. Low-strength material may exist on polymer surfaces owing to a variety of reasons: (i) impurities arising in the polymerisation process; (ii) the low-molecular-weight tail of the molecular-weight distribution; (iii) additives (e.g. antioxidants); (iv) processing aids (e.g. mould-release agents); (v) subsequent contamination of the polymer surface.

At first sight, weak boundary layers would appear to be a likely explanation in the case of polyester film; especially in view of the work of Ross and coworkers [17], in which about 1% of low-molecular-weight material was extracted from polyester film with trichloroethylene. However, the data in tables II and III suggest that weak boundary layers are not the basic problem of polyester adhesion. The bond strengths (shear and direct tensile) achieved with Melinex film were very high compared with Alkathene WJG 11 and were, at the most, a factor of 2 lower than those obtained with aluminium, depending on the type of test carried out. Further, extraction with hot trichloroethylene did not produce a large increase in the bond strength. The fact that the high bond strengths are obtained with an epoxy resin does not mean that low-molecular-weight material does not normally exist on polyester film surfaces. It probably means that the interaction between the polyester and the epoxy resin is sufficiently high to displace the low-molecular-weight material, and the epoxy resin can be strongly adsorbed to the long polymer chains of the polyester film.

4.3. Mechanical Properties

Bonded films (e.g. in the form of a bag) are frequently subjected to peeling forces, whereas direct tensile and shearing forces are generally more important for substrates such as wood and metals. The importance of various mechanical properties of the adhesive in the bonding of flexible substrates has been pointed out by a number of workers. Wake [18, 19] has shown that the degree of curing, and therefore the modulus of a rubber, has an important effect on the peeling force required to separate the rubber from a fabric. When the degree of cross-linking reaches a certain level, the cohesive strength exceeds the strength of adhesion to the substrate, and adhesive failure occurs. Further cross-linking results in a progressive decrease in peel strength, because the increasing modulus of the rubber results in the stress being distributed over a decreasing area of the substrate [18]. Kaelble [20, 21] has discussed in detail various factors, including mechanical properties, that affect the peel strengths of adhesive joints.

One of the objects of this paper is to demonstrate the importance of the mechanical properties of the adhesive in the bonding of polyester film. Analysis of a typical peeling test (see fig. 3) shows that an important requirement of a suitable adhesive is that it should deform in order to reduce stress concentrations in the bond. If the adhesive has a high modulus of elasticity, and low elongation to break, the stress will be concentrated in a small volume of adhesive and on a small area of substrate, and failure of the bond will occur at low applied loads. If the adhesive is flexible, the stress will be distributed over a larger volume of adhesive (and a larger area of substrate), and higher peel strengths will be obtained. However, the adhesive must clearly have sufficient strength to avoid cohesive failure at low loads, as occurs with BEH 6 (table IV).

The importance of flexibility is illustrated by the difference in bond strengths obtained with an epoxy resin and with a caprolactone/hexamethylene adipamide copolymer (BEH 1) on the one hand, and the elastomeric caprolactone polyesters on the other hand (table IV). Very low peel strengths were obtained with Araldite AV 100 and BEH 1, although both these adhesives gave comparatively high bond strengths in shear with Melinex film (table III).

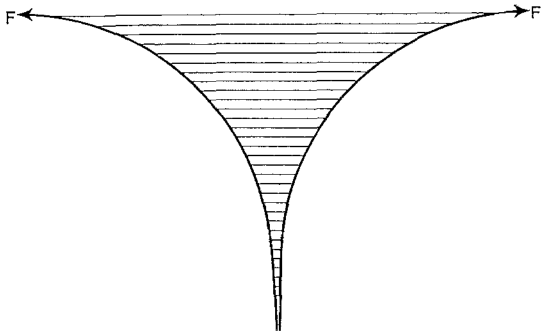

Figure 3 T-peel test (exaggerated).

TABLE IV Peel strengths of Melinex/Melinex bonds formed with various adhesives.

Adhesive	Description of adhesive	Initial modulus (kg/cm^2)	Elongation to break (%)	Peel strength (g/cm)	Type of failure†
BEH 1	Hexamethylene adipamide/ caprolactone copolymer containing 85 moles % lactone (T_m = 93 to 99° C)	1790	270	<150	A
Araldite AV 100 1 Araldite HV 100 1	Cross-linked epoxy resin	~25 000	~5	<150	A
Elvax 260	Ethylene/vinyl acetate copolymer	95	1050	<150	A
Elvax 260 2 Poly-pale Ester 10 1	Copolymer plus resin ester	—	—	890	A
BEH 2	Ethylene terephthalate/caprolactone copolymer	165	730	3210	A + C
BEH 3	Ethylene terephthalate/caprolactone copolymer	50	1300	3920	A + C
BEH 4	Ethylene terephthalate/ethylene isophthalate/caprolactone terpolymer with high elastomeric character	—	—	2650	A + C
BEH 5	Ethylene terephthalate/ethylene isophthalate/ caprolactone terpolymer with high elastomeric character	—	—	5410*	C
BEH 6	Ethylene terephthalate/ caprolactone copolymer containing 68.8 moles % caprolactone – cohesive strength low cf. BEH 2	—	—	890	C

*tested at 35° C
†A – apparent adhesive failure; C – cohesive failure

The effect of testing temperature (table V) also illustrates the importance of mechanical properties of the adhesive. At 30° C, the terpolymer is insufficiently flexible, and apparent adhesive failure occurs at a comparatively low level. The bond strength reaches a maximum at approximately 35° C and then starts to decrease with increasing temperature owing to the decreasing cohesive strength of the adhesive. The importance of mechanical properties is again illustrated by the results in table VII, which gives the bond strengths obtained with a number of samples taken from an autoclave during the preparation of a caprolactone/ ethylene terephthalate copolymer. The early samples, which have low molecular weights, have low elongations to break and low breaking stresses, and consequently gave low bond strengths. The peel strengths rose to a maximum value when the reduced viscosity of the copolymer was about 0.6 dl/g.

TABLE V Effect of testing temperature on the peel strengths of Melinex/Melinex bonds formed with the terpolymer BEH 5.

Testing temperature (° C)	Peel strength (g/cm)	Type of failure
30	1910	Apparent adhesive failure
35	5410	Cohesive
40	3440	,,
45	2620	,,
55	890	,,

The picture so far is fairly clear. However, the results in table VI indicate that other specific effects can dominate the situation. Table VI shows that the bond strengths obtained with BEH 2 fall dramatically with ageing at room temperature and this is accompanied by a loss in clarity of the adhesive. The rate of cooling of the adhesive joints can also have a very pronounced effect in the case of BEH 2. These observations cannot be accounted for in terms of the bulk properties of the adhesive, as the change in mechanical properties under these different conditions is in fact fairly small. It seems more likely that regions of high stress are produced (probably near the interface) during the crystallisation process which takes place over a period of time, or with slow cooling in the case of BEH 2 (table VIII). This is supported by the fact that the terpolymers BEH 4 and

TABLE VI Effect of ageing and of the rate of cooling on the peel strength of Melinex/Melinex bonds.

Adhesive	Description of adhesive	History of bond	Peel strength (g/cm)	Type of failure
BEH 2	Ethylene terephthalate/caprolactone copolymer	Bond cooled to room temperature over a period of 1 min and tested 24 h later	3210	A + C
,,	,,	Bond cooled to room temperature over a period of 1 min and tested 5 days later	<150	A
	,,	Bond cooled to room temperature over a period of 1 h and tested 24 h later	<150	A
BEH 4	Ethylene terephthalate/ethylene isophthalate/caprolactone terpolymer with high elastomeric character	Bond cooled to room temperature over a period of 1 min and tested 24 h later	2650	A + C
,,	,,	Bond cooled to room temperature over a period of 1 min and tested 5 days later	3380	A + C
,,	,,	Bond cooled to room temperature over a period of 1 h and tested 24 h later	3560	A + C
,,	,,	Bond cooled to room temperature over a period of 1 min and tested 27 days later	3260	A + C
BEH 5	A terpolymer similar to BEH 4	Bond cooled to room temperature over a period of *c*. 1 min and tested 24 h later	1910	A
,,	,,	As above, but tested after 8 days	2030	A

TABLE VII Effect of η/c^* on the peel strengths of Melinex/Melinex bonds.

Adhesive	η/c^*	Peel strength (g/cm)	Type of failure	Initial modulus (kg/cm^2)	Elongation to break (%)
Sample 1	0.25	90	C	180	40
2	0.27	180	C	—	—
3	0.28	360	C	—	—
4	0.32	890	C	—	—
5	0.34	800	C	170	80
6	0.37	1160	C	—	—
7	0.53	1960	A + C	—	—
8	0.64	3210	A + C	165	730

$^*\eta/c$ (η = specific viscosity; c = concentration) refers to a 0.5% solution in ortho-chlorophenol at 25° C. The samples were taken from the autoclave during the preparation of the caprolactone/ethylene terephthalate copolymer BEH 2. ($\eta = (t - t_0)/t_0$, where t is the flow time of a solution of the polymer at a concentration c g/dl of solvent through a viscometer, and t_0 is the flow time of the same volume of pure solvent through the same viscometer under the same conditions.)

TABLE VIII Crystallinity data.

Polymer	Description of polymer	Thermal history	Crystallinity (%)
BEH 2	Ethylene terephthalate/ caprolactone copolymer	Cooled from 150° C to room temperature over a period of *c.* 1 min. X-ray measurement made 24 h later	Amorphous
,,		As above, but X-ray measurement made after 5 days	20 ± 3
,,	,,	Cooled from 150° C to room temperature over a period of *c.* 1 h. X-ray measurement made 24 h later	19 ± 3
,,	,,	As above, but measurement made after 5 days	20 ± 3
BEH 5	Ethylene terephthalate/ethylene isophthalate/caprolactone terpolymer	Cooled from 150° C to room temperature over a period of *c.* 1 min. X-ray measurement made 24 h later	Amorphous
,,	,,	As above, but measurement made after 5 days	Amorphous
,,	,,	As above, but measurement made after 9 days	Amorphous
BEH 4	,,	Cooled from 150° C to room temperature over a period of *c.* 1 min. X-ray measurement made 24 h later	Amorphous
,,	,,	As above, but measurement made after 5 days	Amorphous

BEH 5, which remain amorphous, do not show any decrease in bond strength with time or with reduced rate of cooling.

It is interesting to note that, despite the fact that Elvax 260 has similar mechanical properties to a number of the successful caprolactone polymers, the bond strengths obtained with Melinex are very much lower (table IV). This is presumably due to the fact that the specific interaction between Melinex and Elvax 260 is not sufficiently high to enable the adhesive to displace the region of low molecular weight that exists between the Elvax 260 and the polyester film. It is interesting to note that the addition of Poly-pale Ester 10, which is the glycerol ester of polymerised wood resin, causes a large increase in bond strength (table IV). It is unlikely that these observations can be explained by differences in viscosity.

5. Conclusions

(*a*) Weak boundary layers and poor "wetting" are not serious problems with poly(ethylene terephthalate) film.

(*b*) Although pre-treatment of polyester film may lead to improved bond strengths, values, satisfactory for most purposes, can be obtained without such pre-treatment. In other words, work should be directed at the adhesive rather than the substrate.

(*c*) It would appear that important characteristics for a satisfactory adhesive for poly(ethylene terephthalate) film are that the adhesive should have a low modulus, high breaking stress, high elongation to break, and possess groups that give high specific interaction with the polyester.

(*d*) Particular service requirements (e.g. good clarity and good temperature resistance) will also be necessary in many cases, and it is often necessary to compromise between maximum bond strengths and these requirements.

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