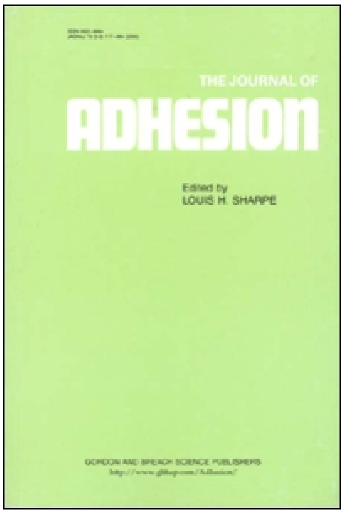

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Adhesive Strength of Deformed Epoxy and Polyester Coatings

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The adhesive strengths of a soft, ductile polyester paint and a stiff, brittle epoxy resin on metal substrates equibiaxially strained to different levels were investigated by pull-off testing. The stress state in the samples after straining was estimated from relaxation tests on unsupported films. It was found that the epoxy behaved elastically at low strains and plastically at higher strains, whereas the polyester responded plastically at all levels of imposed strain. The pull-off stress of the polyester decreased strongly with increasing strain, indicating the formation of defects at the interface. No influence of the elastic strain in the epoxy coating on the pull-off stress could be detected. In both the epoxy and the polyester the location of failure moved towards the interface with increasing strain. After the onset of interfacial failure, the increase in area fraction interfacial failure with strain was found to proceed similarly in both materials.

Keywords: Ductile polyester coating; brittle epoxy coating; metallic substrates; equibiaxial strains; peel and pull-off tests; failure locus; stress state; elastic deformation; plastic deformation

INTRODUCTION

As a consequence both of rising environmental concern and the demand for quicker and more efficient coating processes, the use of

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*Corresponding author.

prepainted metallic sheet is increasing. In this application the coating is applied to the substrate before it has received its final shape, something that typically takes place through a metal forming operation. A coating intended for use on prepainted metallic sheet must, thus, be capable of undergoing the often large deformations occurring during forming without losing either its appearance or its protective properties.

Schematically, the forming operation consists of straining the prepainted sheet, resulting in plastic deformation and an increase of the surface area of the metallic substrate. The coating accommodates the imposed strain by a mixture of elastic deformation and plastic flow. The proportions between elastic and plastic response are determined by the viscoelastic properties of the coating. A typical coil-coating material has a low crosslink density and a glass transition temperature (T_g) close to the forming temperature (usually room temperature) and will, therefore, exhibit extensive plastic flow. As opposed to this, coating materials with higher T_g's and crosslink densities, such as epoxies and acrylates, can be expected to be less prone to plastic flow and instead respond elastically to the imposed strain.

The adhesion of a coating to its substrate is a basic property, essential to the protective as well as the aesthetic functions of the coating [1]. The experimental determination of adhesion is difficult, since there is no single parameter corresponding to adhesive strength. Two often used tests are the peel and pull-off tests [1,2]. The peel test requires a strong, flexible coating whereas the pull-off test is applicable also to softer or more brittle coatings. It is widely recognised that elastic energy stored in a coating affects the effective, measurable adhesion of the coating to its substrate [3,4,5]. Ideally, the residual elastic strain in considered to represent an internal energy which is released on separation of the film from the substrate, thereby reducing the work required to perform the separation. The amount of stored energy and the corresponding decrease in work of adhesion as a function of residual strain can be calculated using elastic models. Croll [3] and Farris *et al.* [4], using pull-off and peel tests, have shown that predictions obtained by this kind of analysis agree well with experimentally measured adhesive properties for thermoplastic styrene and acrylic coatings as well as polyimides. However, discrepancies between theory and experiment were found in some cases, and attributed to deviations from linear elastic fracture behaviour such as plastic (non-recoverable) deformation.

In the present work, the adhesive strength of a soft, ductile polyester paint and a stiff epoxy resin on metal substrates equibiaxially strained to different levels is investigated using the pull-off test. The stress state in the samples after straining is estimated from relaxation tests on unsupported films, and the influence of elastic deformation, plastic flow and increase in substrate surface area on the adhesive strength of the two coatings is discussed.

EXPERIMENTAL

Materials

The polyester coating was a commercial polyester-based system intended for coil coating applications, delivered by Akzo Nobel Coatings, Sweden. The epoxy was a stoichiometric mixture of the diglycidyl ether of Bisphenol F (**1**) and 2,2-di(4-aminocyclohexane) propane (**2**), both received from Ciba Geigy, Switzerland. The epoxy and amine monomers are presented in Figure 1. The substrate material was 0.7 mm thick low alloyed carbon steel, metallized with 10 μm zinc for the polyester and uncoated for the epoxy.

Methods

Polyester-coated metal sheet was obtained from the production line at Swedish Steel (SSAB), Sweden. In the industrial process the substrate was coated with 6 μm primer and 18 μm topcoat, cured twice at 240°C for 30 s each time. To prepare the epoxy samples, the epoxy-amine

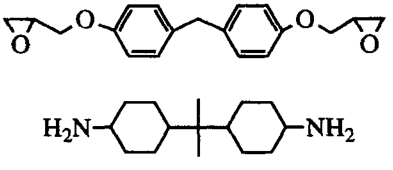


FIGURE 1 Epoxy (**1**) and amine (**2**) monomers.

mixture was applied to the metal sheet and cured at 140°C for 60 minutes. The thickness of the epoxy coating was about 50 μm. The coated sheets were stretch formed, using a cylindrical punch with a flat bottom, in an Erichsen press at low rates (≈ 0.1 mm/min.). The straining was equibiaxial and the strain levels were 0.22, 0.32 and 0.39 for the polyester and 0, 0.09, 0.15 and 0.25 for the epoxy, all in terms of true thickness strain.

Pull-off tests were performed by attaching the ends of cylindrical rods (diameters 30 and 40 mm) to the coating film and the bottom of the steel substrate using a cyanoacrylate adhesive, and then pulling the samples to failure in a tensile testing machine at a rate of 1 mm/min. Using a narrower rod on the coating ensured failure on this side of the samples. The tests yielded two values: a maximum pull-off stress and the area fraction of interfacial failure at the coating-substrate interface, the latter estimated by image analysis of the fracture surfaces.

The relaxed response to deformation of the two coatings was characterised by subjecting unsupported films to different strain levels in a tensile testing machine and measuring the recoverable and non-recoverable components of the total, imposed deformation. The films were typically 15 mm long, 10 mm wide and 0.15 mm thick. They were strained at a rate of 0.1 mm/min and the strain held constant until the stress had fallen to an approximately constant level, which required between 1 and 24 hours. The strain was then reduced until the stress became zero, and the ramaining strain taken to be the non-recoverable component of the total deformation. The difference between the total and the non-recoverable strain yielded the recoverable strain component.

STRESS STATE AFTER STRAINING

The recoverable and non-recoverable strain as a function of total imposed deformation is shown for the polyester in Figure 2. As can be seen, the recoverable stain is only a small fraction of the total strain and is virtually independent of the level of imposed deformation, whereas the non-recoverable deformation increases linearly with total, imposed deformation. Hence, the polyester flows plastically with little

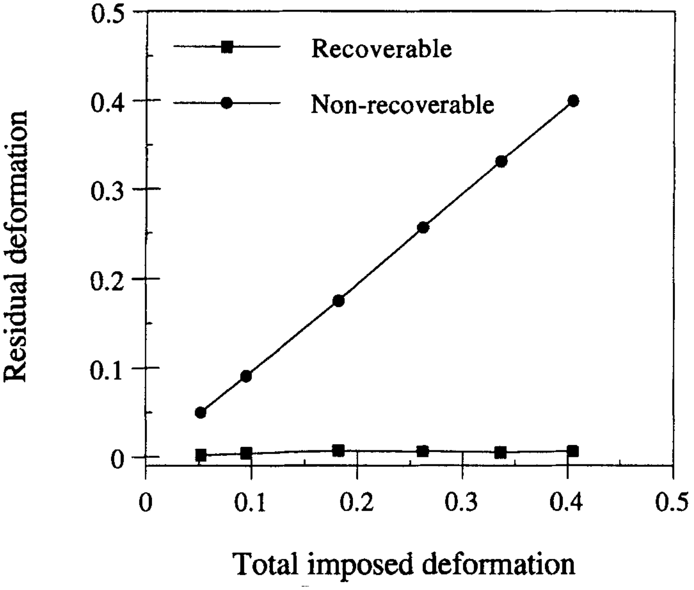


FIGURE 2 Recoverable (elastic) and non-recoverable deformation as a function of total imposed strain for unsupported films of the polyester material in uniaxial tension.

or no strain hardening. The behaviour of the epoxy, depicted in Figure 3, shows it to be less ductile than the polyester. The imposed deformation is almost completely recoverable at low strains, and the non-recoverable component is consequently small. At higher strains the recoverable component shows a tendency to level off and the non-recoverable deformation increases dramatically. The behaviour at higher strains, *i.e.* above 0.1, could not be observed since the samples failed. However, the elongation at break was significantly higher in the samples strained in biaxial tension, presumably due to inhibited necking. This made it necessary to estimate the behaviour also at these levels. By taking the material to be elastic-plastic with some strain hardening (as indicated by the stress-strain behaviour, curves not shown here), the data in Figure 3 can be extrapolated to higher strains. Furthermore, if it is assumed that the strain hardening is linear and that the yield point of the elastic-plastic behaviour is below 0.1 total deformation, linear extrapolations, as shown by the dotted lines in Figure 3, can be made. The extrapolations show that whereas

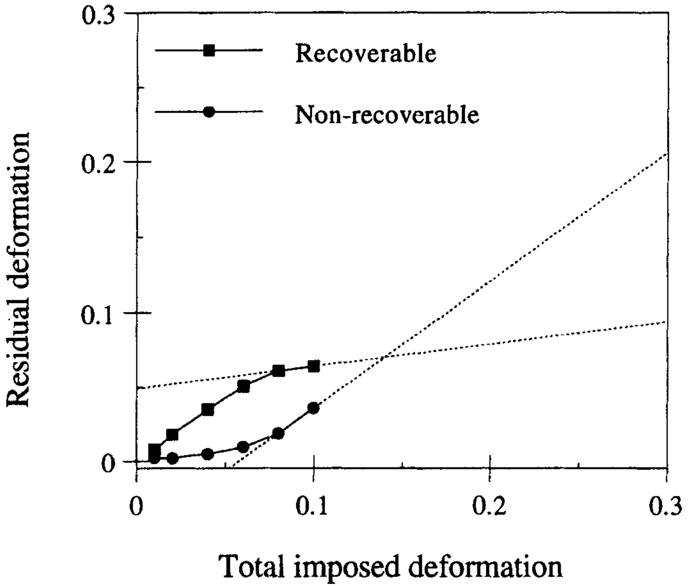
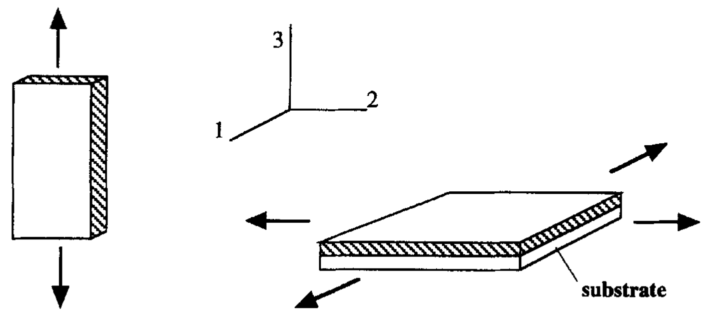


FIGURE 3 Recoverable (elastic) and non-recoverable deformation as a function of total imposed strain for unsupported films of the epoxy material in uniaxal tension. The dotted lines indicate extrapolations.

the recoverable strain dominates at low levels of deformation as discussed above, the non-recoverable strain should first equal and then surpass the recoverable strain as the total deformation increases above 0.15.

The geometry used in the relaxation tests, uniaxial tension, is different from the biaxially strained, plane stress geometry of the adhesion testing samples. The two geometries are depicted in Figure 4 (please note the orientation of the co-ordinate system). However, if the volume is assumed to be constant and the materials taken to be isotropic, the two geometries become equivalent except for the sign of the strain. In both geometries the strains (defined as $\varepsilon = \ln(l/l_0)$) are equal in size in two directions and roughly double in the third direction; $\varepsilon_1 = \varepsilon_2 \approx -0.5\varepsilon_3$. The amounts of recoverable and non-recoverable strain in the biaxially strained samples were estimated from the corresponding values in uniaxial tension at the same *maximum strain*; $\varepsilon_3^{\text{uniaxial}} = -\varepsilon_3^{\text{biaxial}}$. The imposed strain and the estimated recoverable



Uniaxial tension **Equibiaxial tension (plane stress)**

FIGURE 4 Geometries for relaxation tests (uniaxial tension, unsupported film) and adhesion tests (equibiaxial tension, film on substrate). The direction of the imposed deformation is indicated with arrows. Please note the orientation of the co-ordinate system.

and non-recoverable strain components are given for all biaxially strained samples in Table I.

Shown in Table I are also the estimated stress levels in all samples. The stresses arise from the contraction of the coating on cure and cool-down (cure stress) as well as from the elastic strain induced by the deformation of the substrate. The stress level, σ_i, was taken to be the sum of the contributions from the stress present after cure, σ_{cure}, estimated from material data [6] and the recoverable biaxial strain,

TABLE I Samples for adhesion testing and results of pull-off tests

Material	*Imposed in-plane strain, $\varepsilon_1 = \varepsilon_2$*	*Thickness strain, ε_3*			*Estimated stress in coating** [MPa]*	*Pull-off stess [MPa]*	*Area fraction interfacial failure[%]*
		Total	*Re-coverable**	*Non-recoverable**			
Polyester	0	0	0	0	1	25.0±0.6	0±0
	0.11	−0.22	−0.006	−0.214	7	20.5±1.2	1±1
	0.16	−0.32	−0.006	−0.314	7	18.4±0.7	25±5
	0.195	−0.39	−0.006	−0.384	7	16.9±0.5	72±5
Epoxy	0	0	0	0	7	9.3±3.2	4±4
	0.045	−0.09	−0.062	−0.028	59	8.8±2.8	35±30
	0.075	−0.15	−0.071	−0.079	67	10.6±3.5	77±15
	0.125	−0.25	−0.082	−0.168	79	9.7±2.5	100±0

*Estimated from data in Figures 2 and 3.
**From Equation (1).

$\varepsilon_1^r \approx -0.5\varepsilon_3^r$, according to the following expression [3]:

$$\sigma_i = \sigma_{\text{cure}} + \frac{E\varepsilon_1^r}{(1-\nu)} \tag{1}$$

Here E is the Young's modulus and ν the Poisson's ratio of the coating. It should be noted that Equation (1) was derived for small elastic strains, and that its use in the present case, therefore, is debatable. Table I shows that the predicted stress levels in the polyester are moderate. The cohesive strength of the polyester is roughly 30 MPa and the elongation at break about 1% in uniaxial tension. The imposed strain and the predicted stress in the film are, thus, far below the ultimate values for the polyester, Regarding the epoxy, the estimated stress levels are quite high. The cohesive strength of the epoxy is about 75 MPa and the extension at break roughly 0.12% in uniaxial tension. In equibiaxial tension failure was observed at strains just above 0.25, presumably at a stress above 75 MPa due to the strain hardening (the actual stress was not measured since the polymer was on a substrate). The highest strain level for the adhesion testing samples was chosen just below the point where failure occurred. The fact that the estimated stress level in the most strained sample is comparable with the strength of the material (see Tab. I) is, thus, an indication that the stress estimation is accurate.

ADHESIVE STRENGTH

The adhesive strength of the coatings was evaluated with a pull-off test. This test is straightforward and suitable also for soft or brittle materials which are unable to withstand a peel test. There are some drawbacks with the pull-off test, however, in that the joint geometry produces a triaxial stress state in the coating as well as stress concentrations at the edges of the joint [7]. As shown by Adams and Coppendale, the stress concentrations may cause premature failure in brittle materials and, thus, lead to an underestimation of the adhesive strength. Conversely, the triaxial stress state may suppress yielding in ductile materials which, instead, leads to an overestimation of the strength [8]. The pull-off tests gave two values; (i) the maximum stress and (ii) the location of failure, expressed as area fraction of interfacial failure, which refers to the coating-substrate interface. In all cases, failure was divided between the coating–substrate interface and either the coating (polyester samples) or the cyanoacrylate adhesive (epoxy samples). The results of pull-off tests on the samples strained to different levels are shown in Table I.

Regarding the *polyester*, it may be seen that as the level of strain increases, the pull-off stress gradually decreases. In the case of an elastic material failing in a brittle manner, the pull-off stress, σ, is related to the fracture strength, G, through

$$\sigma = \left(\frac{2KG}{t}\right)^{1/2} \tag{2}$$

where K is the bulk modulus of the coating and t the thickness of the coating layer [3]. The high testing rate and the small coating thickness makes elastic behaviour and brittle failure probable, in spite of the ductility exhibited by the polyester in the relaxation tests. According to Equation (2) the pull-off stress should increase as the thickness of the coating decreases if the fracture strength remains unchanged. As the samples are strained the thickness of the coating decreases and the fracture strength changes. The change in thickness is given by the thickness strain according to

$$t = t_0 e^{\varepsilon_3} \tag{3}$$

where t_0 is the thickness before straining. The fracture strength can be assumed to depend on the increase in surface area on straining. It can easily be shown that the area of the base material increases with thickness strain: [9, 10]

$$A = A_0 e^{-\varepsilon_3} \tag{4}$$

Here A_0 is the area before straining. It is hypothesized that the fracture strength depends on the strength of the unstrained interface, G_0, and the relative increase in area on straining according to

$$G = G_0 \left(\frac{A}{A_0}\right)^n. \tag{5}$$

For purely interfacial failure, G is the strength of the interface and the exponent n can be described in terms of change in bond density. Consider an unstrained interface with a certain number of bonds. Three things might happen on straining: (1) no bonds are destroyed or created, in which case only a geometric "dilution" will occur and $n = -1$; (2) bonds are destroyed by the imposed strain and $n < -1$; (3) bonds are created as the surfaces newly formed on straining interact and $n > -1$. $n = 0$ would correspond to a situation where a sufficient number of new bonds were created to keep the bond density constant. The present case is complicated by the fact that failure does not occur excusively at the interface, which means that G and, therefore, also n will depend on a combination of the cohesive and adhesive strengths. If the deformation of the coating takes place without creation of defects, however, the cohesive strength should be unaffected by deformation and the changes in G and n primarily due to what happens at the interface. Combining Equations (3)–(5) and substituting into Equation (2) yields

$$\sigma = \left[\frac{2KG_0}{t_0}\left(\frac{A}{A_0}\right)^{n+1}\right]^{1/2} = C\left(\frac{A}{A_0}\right)^{(n+1)/2} = \sigma_0\left(\frac{A}{A_0}\right)^{(n+1)/2} \qquad (6)$$

where σ_0 is the pull-off stress of the unstrained sample. If the pull-off stress is plotted as a function of relative increase in area, the exponent and n can be determined. Such a plot for the polyester is shown in Figure 5. As can be seen, the experimental data fit Equation (6) with $n = -3$ very well. The low value of n is an indication that the decrease in adhesive strength is more than a geometric effect, *i.e.* that defects are created and/or enlarged by the imposed deformation.

Regarding the *epoxy*, it can be seen in Table I that the pull-off stresses in general were low and the variations between identical samples were large. One reason for this could be the brittle nature of the epoxy coating in combination with the stress concentrations occurring in the pull-off test. The pull-off stress as a function of relative increase in area on straining is shown in Figure 6. As can be seen, n can not be determined decisively. $n = -1$ gives the best fit, but values of n both above and below -1 fall within the limits of the experimental data. The significant amounts of recoverable deformation present in the strained epoxy coatings suggests that an influence of elastically

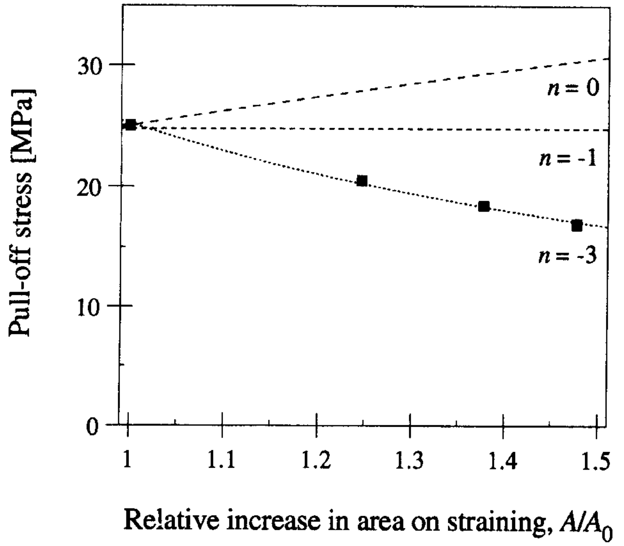


FIGURE 5 Observed pull-off stress *versus* relative increase in area on straining for the polyester samples (■). The dotted lines correspond to Equation (6) with different values of *n*.

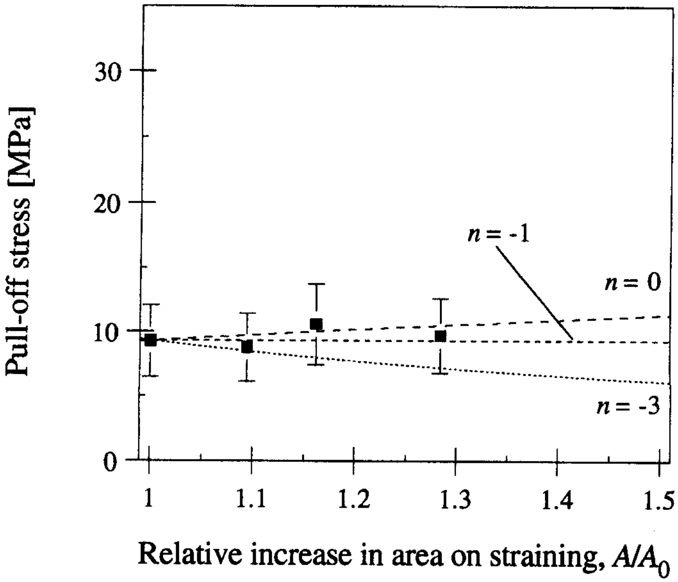


FIGURE 6 Observed pull-off stress *versus* relative increase in area on straining for the epoxy samples (■). The dotted lines correspond to Equation (6) with different values of *n*.

stored energy on the measurable adhesive strength might be detectable. Croll [3] performed pull-off tests on acrylate coatings with different thickness and known stress levels and showed that for purely interfacial failure the effective strength was reduced by the stress in the coating according to

$$G = G_i - \frac{t\sigma_i^2}{E}(1 - \nu), \tag{7}$$

where G_i is the strength in the absence of stress. In the present study, purely interfacial failure occurred at the highest level of imposed strain. Using the data in Table I permits G_i for the most strained sample to be calculated from Equation (7). If G_i is assumed to be roughly the same for all samples (in reality it is probably higher for the less-strained samples) expected values of G and pull-off stress for the less-strained samples can be calculated from Equations (7) and (2). The expected pull-off stresses for such an imagined, entirely interfacial failure become 115, 75 and 60 MPa for the samples strained to 0, 0.09 and 0.15, respectively. These values are far above the cohesive strength of the cyanoacrylate adhesive (30 MPa), which means that failure should have occurred exclusively in the adhesive in all samples except at the highest strain level. In reality, significant failure at the interface was observed also at much lower levels of deformation (see Tab. I). G_i is, thus, not as high as predicted by Equation (7) or, conversely, the elastic energy stored in the coating does not reduce the adhesive strength as expected. In fact, considering the geometry of the pull-off test it can be argued that the use of Equation (7) is questionable. This expression assumes that all elastic energy in the coating is released upon removal from the substrate, but since the coating remains attached to the rod it should retain a major part, if not all, of its elastic energy. The amount of energy released should increase as the thickness of the coating increases and/or the diameter of the rod decreases, since the coating then becomes more free to deform laterally. Croll [3] used rods of 7 mm diameter and acrylate coatings of 100–300 μm thickness, which can be compared with the 30 mm diameter and 50 μm thickness used in the present study. Furthermore, Croll also performed tests on thinner styrene coatings (10–20 μm), and found that Equation (7) did not apply. He explained this with the high flexibility and low adhesion of the styrene coatings, and did not discuss the influence of test geometry on the amount of energy released. It may be suspected, however, that it is the ability of the coating to deform laterally in the test rather than other factors that determines whether Equation (7) will apply or not. It is also worth noting that the assumption of complete energy release probably is more justified in the case of a peel test, and several studies sucessfully relating peel strength to internal stresses have been reported [3,4]. Unfortunately, the properties of the coatings in the present study did not permitt peel tests to be performed.

Table I shows that the location of failure, as indicated by the area fraction of interfacial failure, moves towards the interface with increasing imposed deformation for both the epoxy and the polyester. This suggests that the cohesive strength of the coating is less affected by the imposed strain than is the adhesive strength, *i.e.*, the strength of the interface. The area fraction of interfacial failure as a function of area increase on straining is shown in Figure 7. It can be seen that the

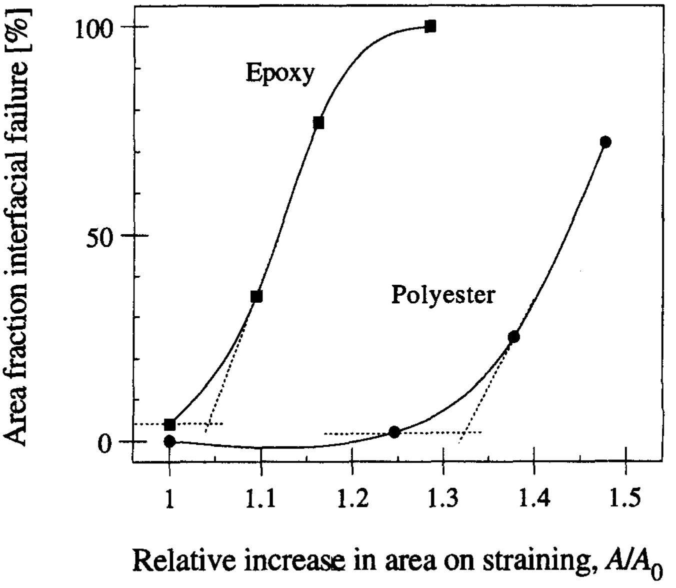


FIGURE 7 Area fraction interfacial failure *versus* relative area increase on straining for the epoxy and polyester samples. The intersections of the dotted lines indicate estimated onsets of interfacial failure.

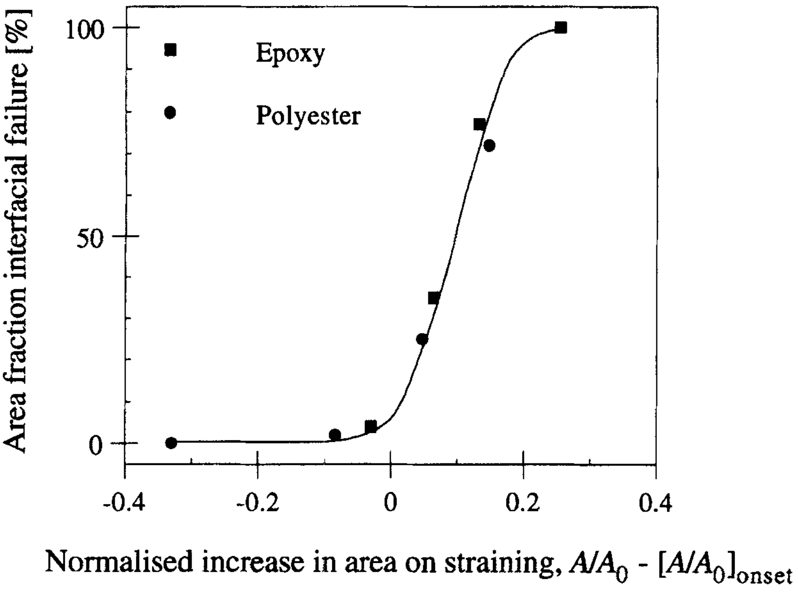


FIGURE 8 Area fraction interfacial failure *versus* normalised relative area increase on straining for the epoxy and polyester samples.

evolution is similar for the two coatings, although the rise in area fraction occurs at lower strains in the epoxy. In the polyester the initial straining of the substrate does not lead to an appreciable amount of fracture at the interface. Indicated by the intersection of the dotted lines in Figure 7 are estimated onsets of interfacial failure, $[A/A_0]_{onset}$. These points can be seen as the points where interfacial failure begins to occur. The value of the onset will depend on the relation between cohesive and adhesive strength in the materials. Interfacial failure will occur when the interfacial strength is lower than the cohesive strength of both the coating and the adhesive. The epoxy has a high cohesive strength compared with the polyester, but the cohesive strengths of the polyester and the adhesive are comparable. Thus, the early onset of interfacial failure in the epoxy is an indication either that the unstrained interface is weaker in the epoxy than in the polyester or that the epoxy interface is more sensitive to straining. The values of pull-off stress did not suggest that the epoxy is more strain sensitive than the polyester. If the curves in Figure 7 are normalised with respect to the onset, *i.e.* presented as a function of $A/A_0 -$

$[A/A_0]_{\text{onset}}$, they reduce to a single curve as shown in Figure 8. This indicates that once the strain is sufficient to initiate failure at the interface, the continued weakening of the interface with increasing strain proceeds similarly in the two materials. In other words, the sensitivity towards straining appears to be similar for both interfaces, in spite of the very different mechanical characteristics of the two coatings, and the early onset in the epoxy thus points to a weaker unstrained interface. Furthermore, the similarity in behaviour between the materials is an indication that n for the two systems also should be similar. The mechanism of the break-down of the interface at higher strains thus seems to be largely independent of the properties of the coating.

CONCLUSIONS

The stress state in equibiaxially strained coatings on metallic substrates can be estimated from uniaxial relaxation tests on unsupported films. Comparing a ductile polyester and a brittle epoxy coating shows that the polyester deforms in a purely plastic manner at all strains, whereas the epoxy responds elastically at low strains but exhibits significant plastic flow at higher imposed strains.

The pull-off stress of the biaxially strained polyester coatings was found to be inversely proportional to the area increase on straining raised to the third power, indicating a gradual growth of defects at the interface with increasing strain. The pull-off stress of the biaxially strained epoxy coatings exhibited significant variations between samples, which made it difficult to draw any precise conclusions. It proved impossible to relate the elastic energy stored in the epoxy coatings to the measurable pull-off stress, presumably due to the restricted lateral contraction of the coating in the test.

The increase in area fraction of interfacial failure with increasing strain was found to proceed similarly in both coatings, as indicated by the fact that the curves became superposable when normalised with respect to the onset of interfacial failure. This suggests that the breakdown of the interface at high strain levels is largely independent of the properties of the coating.

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