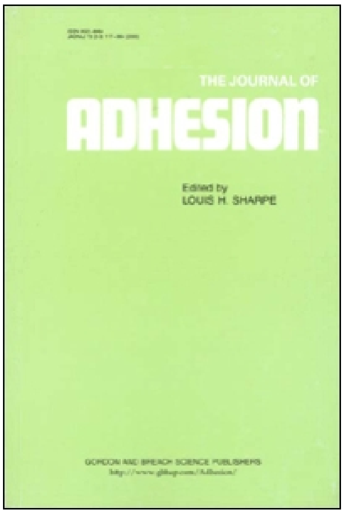

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Peel Adhesion Behaviour of Carboxylic Elastomers

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The introduction of carboxylic acid groups into a poly(butyl acrylate) adhesive greatly increases its bond strength to a glass substrate, as may be seen in a changed force-rate relationship for separation by peeling. By selective carboxylation of the bulk only or the surface only of the adhesive, it is possible to discriminate between bond enhancement by an interfacial effect (presumed to involve interfacial hydrogen bonding) and that by a bulk effect (change in viscoelastic response resulting from carboxylation). The interfacial effect provides a somewhat lower contribution towards the improvement of bond strength than does the bulk effect. Energetic considerations show that the presence of 10% by weight of copolymerised acrylic acid increases the thermodynamic work of adhesion by a factor of about 1.5.

INTRODUCTION

The incorporation of a small proportion of carboxylic groups into a polymer markedly increases its bond strength to rigid polar surfaces, especially hydroxylic surfaces such as those of cellulose or glass. This effect has been well illustrated in earlier studies by Nottage,[1] Hofrichter and McLaren,[2] McLaren and Seiler,[3] Mao and Reegen[4] and, in some cases,[1, 2] proportionality between log (bond strength) and log (carboxylic group concentration) was observed. The very extensive industrial utilisation of the effect has been reviewed.[5] Most results were interpreted mainly in terms of hydrogen bonding and other polar attractive forces at interfaces, and generally neglected effects of any change in bulk viscoelastic state in the carboxylated adhesive.

However, it has been firmly established by many investigators that the behaviour of an adhesive joint in peeling depends strongly upon the bulk

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viscoelastic response of the adhesive (e.g., Kaelble,[6] Gent and Petrich[7]). For joint systems of the kind used in the present work, this dependence has been reviewed[8, 9] and may be illustrated briefly by reference to a typical peel force-rate master-curve, shown in Figure 1. This was obtained by the application of time-temperature superposition to the results of peeling, at 90° angle, a joint comprising a thin, essentially inextensible polyester film bonded by a simple, uncrosslinked poly(butyl acrylate) adhesive to a plane glass substrate[8] (see inset diagrams, Figure 1). As pulling rate increases, the viscoelastic response of the adhesive polymer changes from viscous (region A) through rubbery (region B) to glassy (region C), and the mode of peeling changes accordingly from "cohesive" separation with much filamentation (region A), through "adhesive" separation from glass with little filamentation (region B) to "adhesive" separation from film, with no filamentation and extremely low peel force (region C). In the "stick-slip" peeling region labelled B-C, the recorded force oscillates between well-defined limits (see inset diagram, Figure 1), and is believed to reflect regular alternation between "rubbery" (region B) and "glassy" (region C) modes of behaviour. A narrow "stick-slip" region is also sometimes observed between regions A and B. Light crosslinking of the adhesive eliminates region A and allows region B to extend throughout the lower rates.

As might be expected by analogy with master-curves of other viscoelastic phenomena, a change in the chemical nature or composition of the

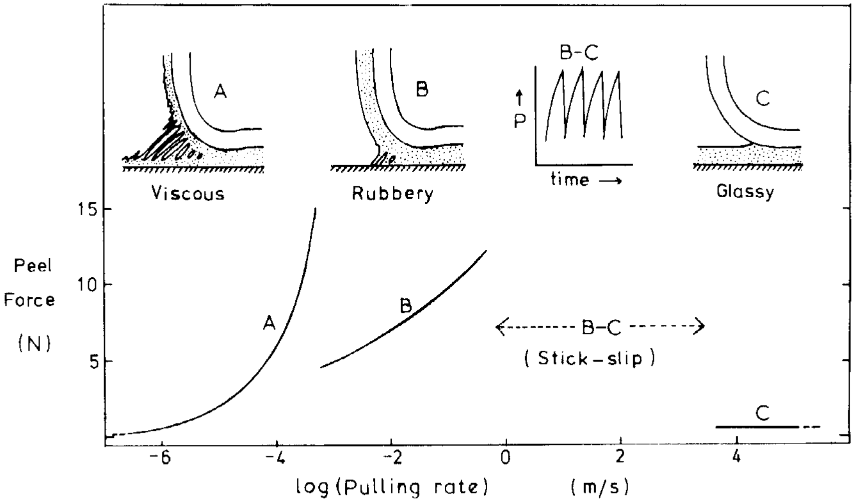

FIGURE 1 Master-curve of peel force v. (log) pulling rate at 296 K for polyester film/poly(butyl acrylate) adhesive/glass substrate. Film and adhesive are each 25 μm thick and 2.54 cm wide. Drawings illustrate the adhesive behaviour in each region.

adhesive (whilst keeping all other factors, including interfacial free energy, constant) will cause a horizontal displacement of the whole master-curve along the abscissa, to an extent reflected by the change in glass transition temperature T_g. This displacement is clearly seen in curves obtained with polyvinyl acetate[9] and natural rubber/resin[10] adhesives.

The mode of peeling of greatest interest is that involving rubbery response (region B) with adhesive separation from glass, since this is the type of separation most commonly encountered with adhesive tapes and elastomeric adhesives generally. The present study concentrates on this "rubbery" mode of peeling and uses lightly cross-linked adhesive in order to extend the range of rates over which it is observed.

It will be clear from the foregoing discussion that the introduction of carboxylic acid groups into a poly(butyl acrylate) adhesive will be expected to affect the force-rate curve (region B) in two distinct ways: first, by increasing interfacial energy, carboxylation is expected to cause a *vertical* upward displacement of the curve (*i.e.* a rise in force from an effect independent of rate); secondly, by increasing bulk cohesive energy, it is expected to raise T_g and cause a *lateral* displacement to the left. Such displacements would, of course, normally be superimposed and indistinguishable in the resultant displaced curve. The aim of the present investigation is to separate the two components of displacement by comparing the peeling behaviour of adhesives which have been carboxylated on the surface (but not in the bulk) with those carboxylated in the bulk (but not on the surface).

JOINT PREPARATION AND TESTING

Adhesives

Two adhesive polymers, poly(*n*-butyl acrylate) and a 90:10 (wt) *n*-butyl acrylate: acrylic acid copolymer, were prepared by benzoyl peroxide initiated polymerisation in benzene solution. Polymerisation conditions were maintained as similar as possible for the two polymers, except for programmed addition of acrylic acid in the copolymer case to allow for different reactivity ratios. After one and a half hours polymer was isolated in approximately 30% yield in each case by precipitation and washing in methanol (homopolymer) or hexane (copolymer). A little homopolymer was added to the copolymer to adjust its acrylic acid content to exactly 10% w/w (16.5% molar), as characterised by volumetric acid value determinations. Glass transition temperatures T_g (D.S.C., 0.066 deg min^{-1}) were found to be 210K and 226K for the homopolymer and copolymer, respectively. The two polymers are referred to as "PBA" and "carboxy-PBA", below.

Joints

Each polymer, with added benzoyl peroxide (2 % wt) was coated from toluene solution on to primed polyester film ("Melinex" type 0, 23 micron, I.C.I. Ltd.) to a dry coating weight of 23 ± 2 g m^{-2}. To effect surface modification, a "supercoating" was applied by spray (approximately 1 % in toluene) to a final dry weight within the range 2–5 % of the overall weight of adhesive. Within this range the supercoating displays a negligible bulk effect during peeling (later). Thus a thin PBA supercoating was applied to a carboxy-PBA adhesive and, conversely, a carboxy-PBA supercoating was applied to a PBA adhesive. Supercoatings, but of the same composition as the bulk, were also applied to adhesives where surface modification was not required. Strips (24.5 mm wide) of the coated films were rolled into contact with clean glass test plates, then heated (393 K, 20 min) to effect cross-linking. Cross-linking serves to increase the range of rates over which "rubbery" peeling is observed.[8]

Peel tests

Joints were peeled at 90° angle on an Instron machine, as represented in Figure 2. Horizontal translation of the glass test-plate maintains the position of the peeling zone. Peel force, P, was measured at seven discrete rates ranging from 1 to 50 cm min^{-1}, at each of six temperatures, T, ranging from 230 K to 248 K. Curves of "reduced" peel force, $P_r = 296\ P/T$, against (log) pulling rate, R, for each temperature were superimposed experimentally to

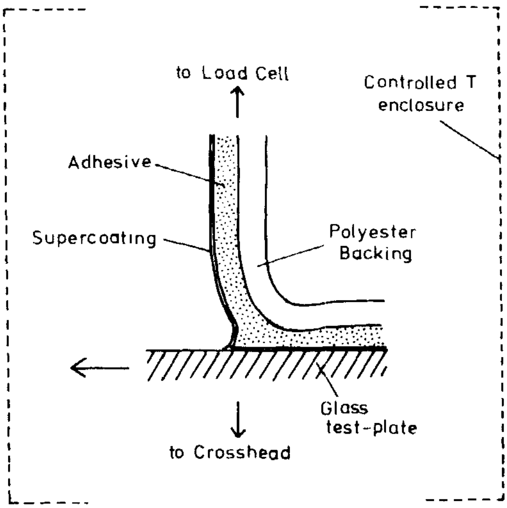

FIGURE 2 Peeling arrangement.

form a "master-curve" of (reduced) peel force against (log) pulling rate at 296 K, as has been described.[8] At the lowest temperatures oscillatory (stick-slip) peeling occurred, and was ignored.

Effect of supercoating weight

Peel force at 296 K and 3 cm min^{-1} was measured for joints using PBA with different weights of (a) PBA and (b) carboxy-PBA supercoating (Figure 3). Supercoating weight has a negligible effect on peel force up to a fractional weight increase of about 1.07, a range within which it was easy to confine the sprayed weight of supercoating. The increase in peel force (ΔP, Figure 3) resulting from the carboxy-PBA supercoating appeared to approach a constant value as supercoating weights reached the limit of detectability. Results obtained from unmeasurably thin supercoatings, not shown in Figure 3, also show the same value, and no intermediate values of peel force were obtained. This was taken as reassurance that mutual mixing of supercoating and base polymer was not occurring to an extent sufficient to produce a "partially-carboxylated" surface.

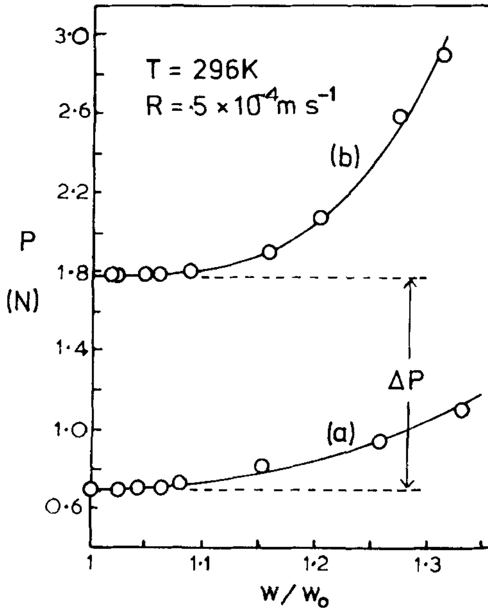

FIGURE 3 Peel force P v. fractional weight increase W/W_0 due to (a) PBA and (b) carboxy-PBA supercoating.

RESULTS AND DISCUSSION

Master-curves formed by the shifted data points are presented in Figure 4 (PBA and PBA with carboxy-PBA surface) and Figure 5 (carboxy-PBA and carboxy-PBA with PBA surface).

The differences between curves (a) and (b) (Figure 4), and between curves (c) and (d) (Figure 5) should reflect only the interfacial effects of carboxylation (i.e. should represent only a *vertical* displacement) since bulk adhesive composition remains unchanged within each pair. That this is so is revealed by the approximate constancy of shift factors, a'_T, within each figure. Each set of shift factors shows a temperature-dependence conforming to that given by the WLF equation and, using "universal" WLF constants, predicts T_g values of 260 K (PBA) and 273 K (carboxy-PBA), in fair agreement with the measured values.

The *lateral* displacements, curves (a) → (c) and (b) → (d), result from a change only in bulk composition, and are best examined in Figure 6, where all four master-curves are shown as line graphs. It is clear that these lateral displacements are not uniform, since curves (a) and (b) show greater curvature than (c) and (d). The curves (a) and (b) may be superimposed by lateral shifting; similarly, curves (c) and (d) will superimpose. However, superposition is not possible between (a) or (b) *and* (c) or (d). These observations suggest that the temperature-dependence of cohesive forces arising from carboxyl groups differs from that of the main cohesive forces.

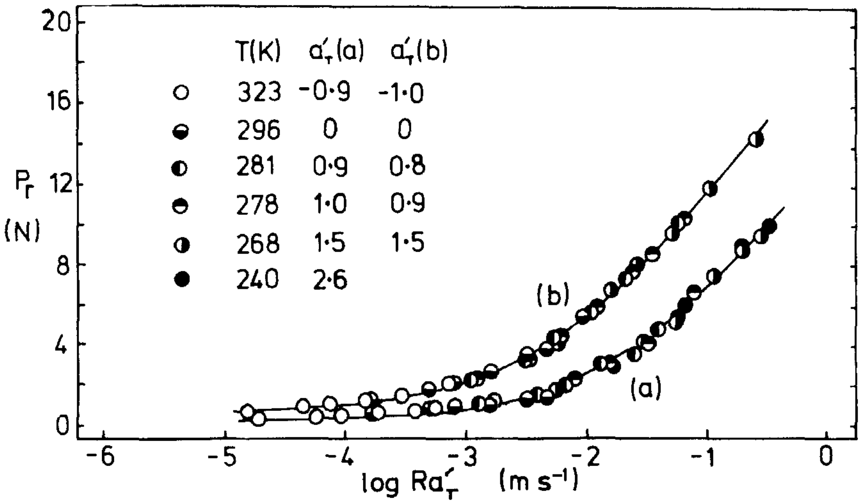

FIGURE 4 Master-curve of reduced peel force P_r v. (log) pulling rate R at 296 K for (a) all PBA and (b) PBA with carboxy-PBA supercoating.

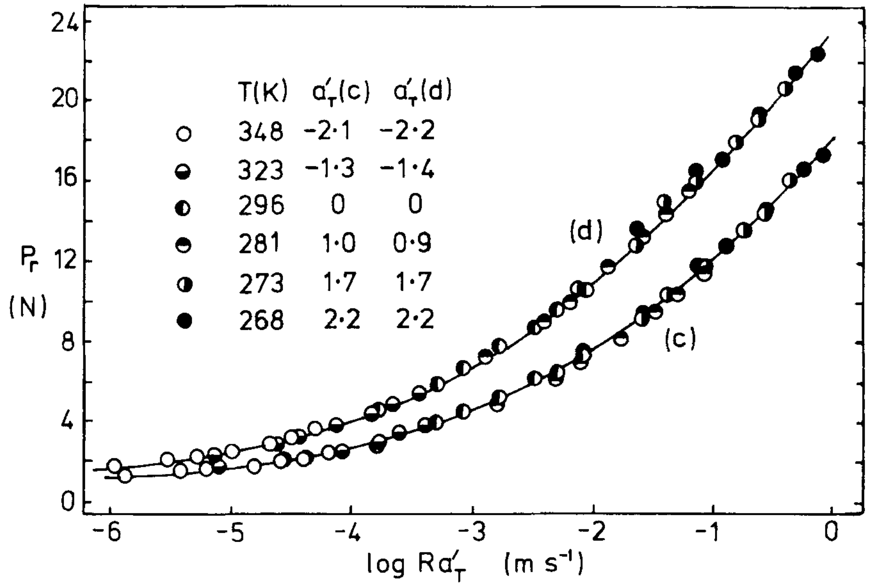

FIGURE 5 Master-curve of reduced peel force P_r v. (log) pulling rate R at 296 K for (c) carboxy-PBA with PBA supercoating and (d) all carboxy-PBA.

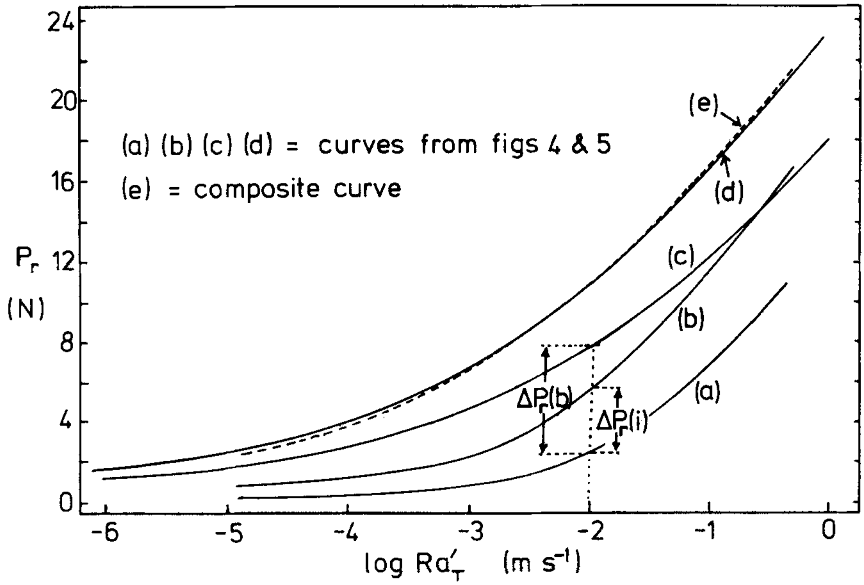

FIGURE 6 Line graphs of curves (a), (b), (c) and (d) from Figures 4 and 5, and hypothetical composite curve (e).

The relative contributions to peel force by interfacial and bulk effects are not constant as rate varies. This may be seen in the increase of ratio ΔP_r(i): ΔP_r(b) (Figure 6) from about 0.3 to 1.1 over the accessible range of rates. Clearly, the bulk effect makes the major contribution up to rate $\log Ra'_T = 0.7$ m s^{-1}, where it is overtaken by the interfacial effect. It is gratifying to note that summation of these individual contributions gives a composite hypothetical master-curve (e) (Figure 6), which closely matches the experimental curve (d).

Following the generalised fracture mechanics approach used by Andrews and Kinloch,[11, 12] the total work of peeling $W_p (= 100\ P_r/2.54$ in J m^{-2}) may be expressed as the product of the work of adhesion W_a (*i.e.* the energy required to overcome intermolecular attractions at the interface) and a dissipation function ϕ to allow for energy expended in bulk viscoelastic processes within the adhesive. It is assumed that negligible energy is dissipated in deforming the polyester film or glass substrate. In the present instance, therefore, the function ϕ is expected to depend only on peeling temperature T, on adhesive strain rate $\dot{\varepsilon} \approx$ pulling rate R, and on an average extent of strain ε within the adhesive during separation. Thus,

$$W_p = W_a \phi(T, R, \varepsilon)$$

and, therefore,

$$\log W_p = \log W_a + \log \phi$$

If it is assumed that T and ε are constant during peeling, so that ϕ depends only on R, it follows that plots of $\log W_p$ against $\log R$ for adhesives of the same bulk but different surface compositions should be displaced vertically relative to one another by a constant interval $\Delta \log W_a$.

In such plots from the present results (Figure 7) it appears that the interval $\Delta \log W_a$ obtained by surface carboxylation of an uncarboxylated adhesive (lines (b) and (a)) is somewhat lower than that obtained by decarboxylation of the surface of a carboxylated adhesive (lines (c) and (d)). Also there is some deviation from constancy of $\Delta \log W_a$, which reduces with increasing $\log R$ for both sets of curves.

These deviations suggest that the assumed constancy of average strain ε is not fully justified. It might be expected that ε would be somewhat greater, due to increased cavitation and/or filamentation, for an adhesive of low modulus (e.g. curve (a) at lowest rates) than for an adhesive of high modulus (*e.g. curve* (d) at highest rates). Thus, the measured interval $\Delta \log W_a$ probably includes a small increment due to $\Delta \log \varepsilon$ which gradually reduces as peeling conditions involve increased adhesive stiffness.

The interval $\Delta \log W_a$ (Figure 7) varies between about 0.15 and 0.30,

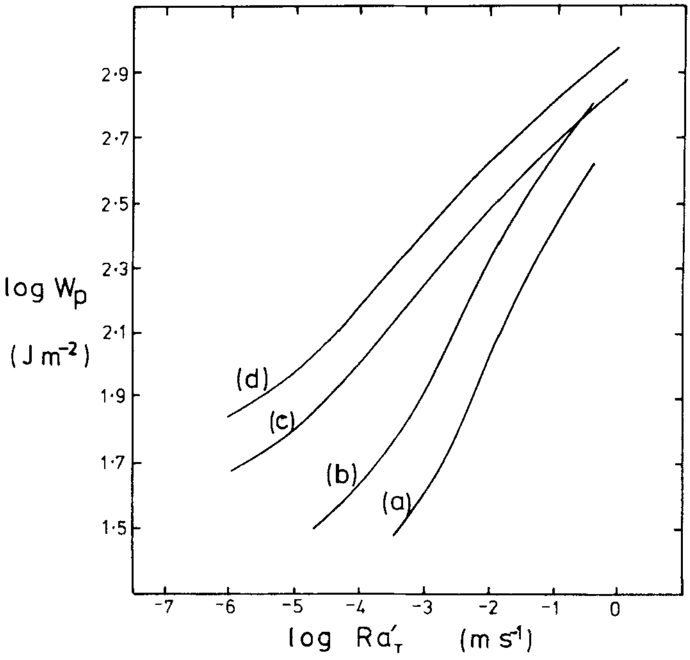

FIGURE 7 Log (work of peeling) W_p versus log (pulling rate) R. Curves (a), (b), (c) and (d) refer to adhesives of Figures 4 and 5.

corresponding to a fractional increase in W_a from surface carboxylation (*i.e.*, W_a (surface carboxylated)/W_a (surface uncarboxylated)) of between about 1.4 and 2.0. The most acceptable values are probably those from curves (c) and (d) at the lower rates, where little filamentation of the adhesive occurs and there is least probability of ductile deformation in the polyester film; Duke[13] holds the view that such ductile deformation of backing films is more common than generally recognised and may contribute appreciably to the work of peeling.

In this region Δ log W_a is constant at 0.18 over a wide range of rates; this suggests a fractional increase in W_a of 1.5, a figure which is not unreasonable in view of the substantially higher dissociation energies of hydrogen bonds compared with those of other intermolecular attractions.

Although these results will not give an absolute value for W_a, it cannot be greater than a few hundred mJ m^{-2}, and is certainly much lower than the lowest measured W_p value (1.6×10^4 mJ m^{-2}). Thus, by far the greater part of W_p represents energy dissipated in deformation processes within the adhesive.

CONCLUSIONS

The increase in peel strength from glass resulting from carboxylation of a poly(butyl acrylate) adhesive is attributable to a combination of at least two separate effects. The first is an interfacial effect presumed to arise from interfacial hydrogen-bonding; the presence of 10% by weight of acrylic acid in the polymer appears to increase thermodynamic work of adhesion by a factor of about 1.5. The second effect arises from a change in the viscoelastic state of the adhesive bulk and generally makes a more important contribution to the increased peel force at a given rate; since this effect is independent of the nature of the interface, it will manifest itself during the peeling of a carboxylated elastomer from any rigid substrate.

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