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Adhesion to Sintered Substrates

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Although the consensus is that various forms of specific adhesion are prevalent in most adhesive systems, the importance of mechanical adhesion should not be overlooked. Cylindrical substrates of stainless steel, both the dense metal and in sintered form, have been bonded with a polyurethane “adhesive” and subjected to torsional shear loading. Overall strain and load at failure are considerably higher with porous substrates and the effective energy of adhesion is typically an order of magnitude greater. Mechanical interlocking of the polymer in interstices of the metallic substrate prevents catastrophic failure after the interface has failed. The behaviour has been modelled by taking the “glueline” to be a “composite” structure consisting both of bulk polymer and connecting fibrils.

KEY WORDS: Mechanical adhesion; interlocking; porous substrate; stainless steel; sintered stainless steel; polyurethane adhesive; adhesion tests; apparent work of adhesion; polymer anchoring.

INTRODUCTION

Adhesion and adhesives have been exploited by mankind for several millenia, but scientific investigation into the mechanisms preventing two attached substrates from falling apart is far more recent. Early interest in the fundamental reasons for adhesion apparently goes back only some 80 years or so when, according to Wake¹, World War I aircraft were being assembled with carpenters' glue and this commodity was expected to become scarce. A replacement would be required and to find a suitable replacement, some understanding of the adhesion mechanism(s) might be useful! McBain and Hopkins² suggested in their “mechanical theory of adhesion” that interfacial strength depends essentially on anchoring of the adhesive, after solidification, amongst the pores and asperities of the rough substrate. The liquid adhesive flows and moulds itself around the tortuous geometry of the solid substrate and, after solvent evaporation, crosslinking or simple cooling below melting point, mechanical interlocking hinders separation of the two phases. Although this theory may adequately explain adhesion to rough materials such as textiles or paper, many cases of strong adhesion are known when the substrate is very smooth and mechanical interlocking cannot satisfactorily explain observed strength—there is even some

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doubt as to whether the anchoring mechanism can explain adhesion to smooth wood, which was at the origin of the theory! McBain and Hopkins², therefore, suggested the concept of "specific" adhesion for which various theories have been proposed since the early days, depending on the substrates and conditions involved. Examples are chemical adhesion³, electrostatic adhesion⁴, adhesion by diffusion⁵ and the adsorption or wetting theory⁶. Many workers contributed to the above notions over a considerable period of time and References 3 to 6 correspond only to examples of early proponents of the various theories. Reference 1, or a more recent review, Reference 7 should be consulted for an overview.

Over the years, theories of "specific" adhesion have had their vicissitudes and although the theory of mechanical anchoring has to some extent regained favour in the context of adhesion to aluminium and titanium alloys⁸, adhesion scientists today generally believe that, in most systems, some form of "specific" adhesion plays the predominant role. Cases in which mechanical adhesion corresponds to the major mechanism are relatively rare and, as a consequence, little attention seems to have been paid to obtaining a better understanding of the potential of McBain and Hopkin's early concept⁹. The present work has aimed at trying to assess the importance of mechanical contributions to overall adhesion by using chemically similar substrates whilst significantly changing the topography. This has been effected essentially by using dense metal substrates as "smooth" adherends and their sintered counterparts as "rough" surfaces.

EXPERIMENTAL

Materials

The materials used in this study were a stainless steel for the adherends and a polyurethane as the "adhesive". Stainless steel cylinders of nominal diameter 20 mm and length 30 mm were produced from a fairly standard material, denoted 316L (containing 0.03% C (max), 16–18% Cr, 10–14% Ni and 2–3% Mo). Both fully dense cylinders and sintered metal cylinders were used for comparison, the latter being supplied by the Department of Mechanical Engineering (Engineering Materials Research Group) at the University of Bradford, U.K. Sintered cylinders were made by heating pre-formed particulate compacts, produced in a mould at *ca.* 600 MPa, to *ca.* 1200°C for *ca.* 6 h. Various particulate sizes were used with an average diameter ranging from 38 to 152 µm leading to total porosity values in the range of 15–35% (interconnected porosity, 4–23%).

The "adhesive" used in this study was a polyester-based thermoplastic polyurethane elastomer, Estane 58271 from B. F. Goodrich. Moulded sheets of polymer produced from the granular material were cut to produce 4 mm thick, 20 mm diameter discs. "Adhesive" bonds were produced by preheating metal cylinders to 180°C for 10 min, placing a polymer disc between them and then applying a load to facilitate polymer penetration (in the case of sintered adherends). Typical pressing conditions corresponded to an applied load of 25 kN at 180°C for 5 minutes.

Apparatus

Various types of adhesion tests have been developed over the years but none is capable of applying a "pure" shear stress distribution to the interface. The nearest to this ideal is the "napkin ring" test suggested by de Bruyne¹⁰ and later developed by others (*e.g.* Refs. 11,12,13). In the present work, a modification of the "napkin ring", or torsional test, has been employed. Instead of two hollowed-out cylinders being bonded together, two full cylinders bonded end to end have been used as the geometry. It is true that one of the intrinsic advantages of the "napkin ring" geometry is lost, *viz.* that of presenting an annular region of small radial extent compared with the outside radius of the cylinders. However, for experimental reasons, it was not practical to use the hollowed-out geometry. Although stress can no longer be considered to be everywhere constant, it does correspond to (almost) pure shear and, at least in the linear elastic domain, is a linearly increasing function of radius. The torsional test used has been described earlier^{13,14} although a few modifications were necessary in the present study (to allow for cylinder/cylinder rather than cylinder/plate geometry). Accurate measurement of relatively large angular displacements was assured using a cam and transducer (LVDT) arrangement.

Tests were effected at constant nominal rate of rotation, $\sim 0.03 \text{ rad.min}^{-1}$, at ambient temperature, $\sim 20^\circ\text{C}$. Applied couple, M , and angular displacement, θ as a function of time, t , were obtained using computer-aided acquisition. Shear modulus, G , of joints (*i.e.* the polymer) could be assessed from the equation:

$$G = \frac{2eM}{\pi r_e^4 \theta} \quad (1)$$

where e is polymer layer thickness and r_e the outer radius of the cylindrical joint. Equation (1) is valid only at the start of loading, as will be explained below.

RESULTS AND INTERPRETATION

In earlier work¹⁵, effects related to impregnation conditions and the depth of polymer penetration into the porous metal structure were considered, but in the present paper we are mainly concerned with differences in mechanical behaviour observed between assemblies made with dense metal and those made with porous substrates, for fixed pressing conditions. As shown in Figure 1, which gives applied couple, M , *vs.* maximum shear strain, γ_{max} (*i.e.* at $r=r_e$), for a bonded assembly of metal (surface) porosity of 22.5% (interconnected 14.5%) and "glueline" thickness, e , of 3.7 mm, and an equivalent dense adherend structure, initial behaviour is similar for joints made with porous and dense substrates, but failure occurs at a much lower value of γ_{max} (and M) in the latter case. In addition, separation between the dense metal and the polymer occurs cleanly and apparently interfacially (although no analysis has been performed to see if small amounts of polymer are left on the metal), whilst fibrils of polymer remain on the porous metal. It is reasonable to assume that the extra mechanical strength obtained in the case of porous adherends is due to the tenacity of the polymer within the porous structure, and the extra

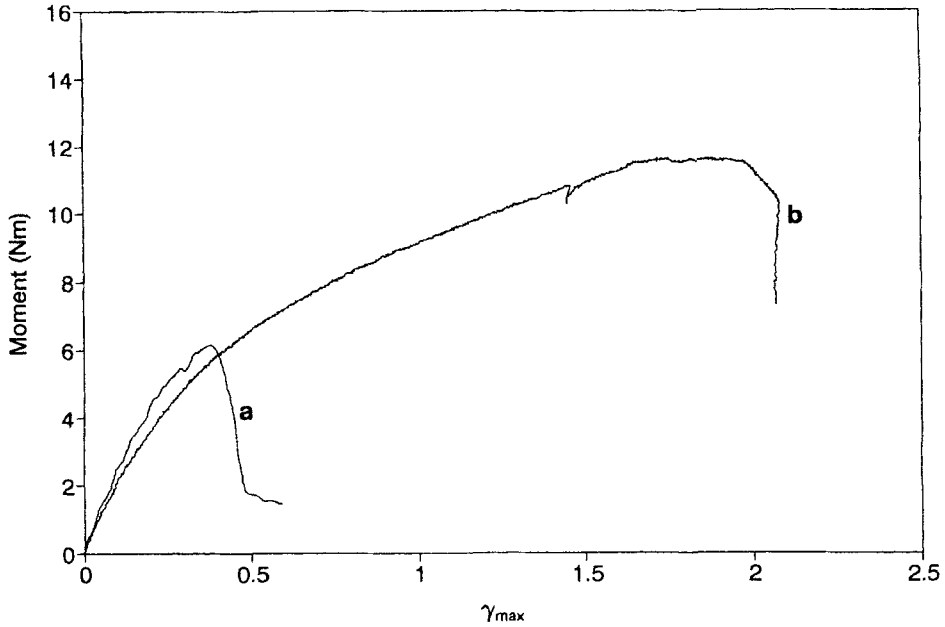


FIGURE 1 Applied couple, M , vs. maximum shear strain, γ_{\max} (at $r = r_e$), for (a) dense metal joint, (b) porous metal joint.

energy required in deforming the polyurethane as the relative rotational displacement of the metal cylinders increases.

Estimate of Apparent Work of Adhesion

We shall first of all estimate the apparent work of adhesion of the two types of systems in question using a simple calculation¹⁵.

The maximum shear strain, γ_{\max} , at $r = r_e$, is related to angular displacement, θ , by:

$$\gamma_{\max} = r_e \theta / e \quad (2)$$

By rotating the joint to failure, the work expended is given by:

$$\bar{W} = \int M(\theta) d\theta = \frac{e}{r_e} \int_0^{\gamma_{\max}(\text{failure})} M(\gamma_{\max}) d\gamma_{\max} \quad (3)$$

and, thus, the apparent work of adhesion, W , is:

$$W = \frac{\bar{W}}{\pi r_e^2} = \frac{e}{\pi r_e^3} \int_0^{\gamma_{\max}(\text{failure})} M(\gamma_{\max}) d\gamma_{\max} \quad (4)$$

The area under M vs. γ_{\max} curves, such as those given in Figure 1, may thus be used to estimate apparent work of adhesion. In the cases shown, W is found to be of the

order of $1\text{--}1.5\text{ kJ}\cdot\text{m}^{-2}$ for dense metal joints and *ca.* $15\text{ kJ}\cdot\text{m}^{-2}$ for porous metal joints. These figures show quite clearly that the adhesion strength of the metal/polymer joints is enormously increased when porous adherends are employed. Some of this increased energy will undoubtedly be due to the fact that interfacial failure with porous adherends requires the creation of more free metal and free polymer surfaces since the real interfacial area is in excess of the geometric equivalent—an effect not present with dense adherends. An increase in the effective value of Dupré's energy of adhesion, W_0 , is thus partially responsible. However, this contribution is believed to be relatively small since the values of apparent energy of adhesion, both for dense and porous substrates, are greater than typical values of W_0 by a factor of approximately 10^4 (or more). It is thought that the major consumer of additional energy in the separation of joints made with porous substrates is extra polymer deformation associated with the fact that the "adhesive" is anchored to the substrate, preventing premature failure. We shall attempt to model this process and its effects.

Model of Anchoring of Polymer and its Contribution to the Apparent Energy of Adhesion

The appearance of failure surfaces of dense metal joints suggests that separation is interfacial, whereas, in the case of sintered metal joints, polymer residue, or fibrils, are apparent on the metal surface. It would seem probable that separation is "clean" on exposed metallic parts even with sintered substrates but that polymer trapped within interstices will not be so easily extracted. In addition, the gradient of M vs. γ_{\max} (or θ) curves for sintered adherends usually decreases at values of γ_{\max} comparable with those observed at failure for dense metal joints (*cf.* Fig 1.). With this evidence, we propose the following simple model of polymer/metal behaviour. We assume that separation between exposed metal and polymer (*i.e.* surfaces as in the dense joint) occurs locally at a given critical value of bulk polymer shear strain, γ_c . Polymer within an interstice, however, is anchored at the bottom, as shown schematically in Figure 2. At γ_c , the exposed metal/polymer interface separates putting shear stress on interstitial polymer. For a "glueline" of thickness e , and assuming separation at only one interface of the joint for simplicity (of course, in reality it may occur at both), we have a metal/metal relative displacement of $\gamma_c e$. After separation, slight retraction of the polymer is assumed to occur such that the anchored polymer is drawn out a distance t , as shown. Since the local stress remains constant (momentarily) and we take the surface fraction of drawn interstitial polymer to be f , we now have a "composite" glueline, mainly constituted of bulk polymer of shear modulus, G , and thickness, e , but partially consisting of a thin layer, of thickness t , of fibrils. The effective modulus of this latter layer is fG . As a consequence, the overall effective shear modulus of the glueline, \tilde{G} , becomes, after interfacial separation:

$$\tilde{G} = \frac{G(e+t)}{(e+t/f)} \approx G \left(1 - \frac{t}{fe} \right) \quad (5)$$

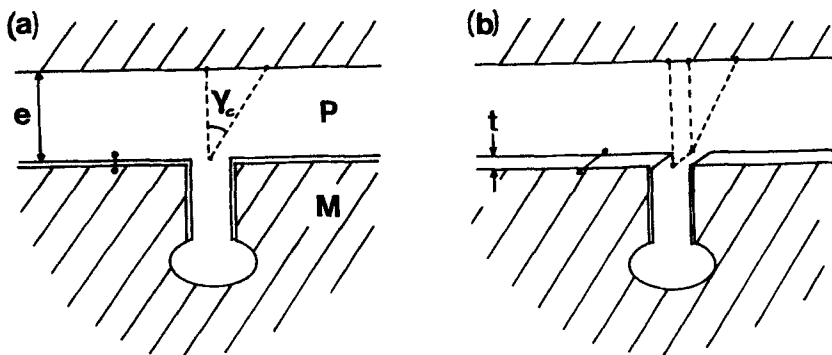


FIGURE 2 Schematic representation of interfacial separation in sintered metal system occurring at local (bulk polymer) shear strain γ_c .

We may now simply write the effective shear stress (τ)/strain (γ) equations for the overall glue-line as:

$$\tau = G\gamma; \quad \gamma < \gamma_c \quad (6)$$

$$\tau = \tilde{G}\gamma + (G - \tilde{G})\gamma_c; \quad \gamma \geq \gamma_c \quad (7)$$

In the case of a torsional joint, we have:

$$M = \int_0^{r_c} 2\pi r^2 \tau(r) dr \quad (8)$$

where r is radial distance from the axis of symmetry. We define a critical value of $\theta = \theta_c$ corresponding to the onset of fibrillar creation at $r = r_c$ (see Fig. 3):

$$\theta_c = e\gamma_c/r_c \quad (9)$$

and, thus, we obtain:

$$M = \int_0^{r_c} \frac{2\pi G\theta}{e} r^3 dr = \frac{\pi G r_c^4 \theta}{2e}; \quad \theta < \theta_c \quad (10)$$

Once θ_c has been attained, henceforth, for $\theta > \theta_c$, the transition between behaviour corresponding to an intact polymer/metal interface (glue-line modulus, G) and a fibril supported interface (effective modulus, \tilde{G}) will occur at a decreasing value of r , denoted r_t . As a result, couple M will be given by:

$$M = \int_0^{r_t} \frac{2\pi G\theta r^3}{e} dr + \int_{r_t}^{r_c} 2\pi r^2 \left[\frac{\tilde{G}\theta r}{e} + (G - \tilde{G})\gamma_c \right] dr \quad (11)$$

and with $r_t = e\gamma_c/\theta$ (cf. equation (9)), we obtain:

$$M = \frac{\pi \tilde{G} r_c^4 \theta}{2e} - \frac{\pi(G - \tilde{G})\gamma_c^4 e^3}{6\theta^3} + \frac{2\pi(G - \tilde{G})\gamma_c r_c^3}{3}; \quad \theta \geq \theta_c \quad (12)$$

Equations (10) and (12) may, thus, be applied to experimental M vs. θ curves and an example is given in Figure 4, corresponding to the sintered metal joint results given in Figure 1. It can be seen that the agreement between experimental results and the theoretical curve is satisfactory. Some approximations have clearly been necessary

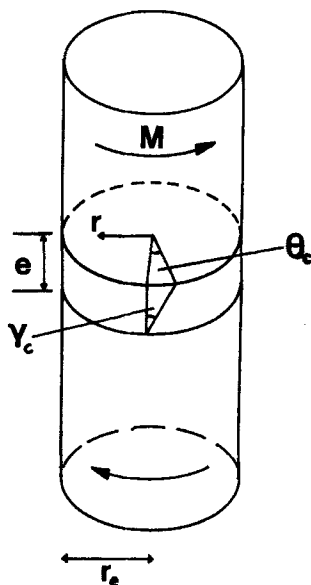


FIGURE 3 Sketch of torsional joint at onset of fibrillar adhesion.

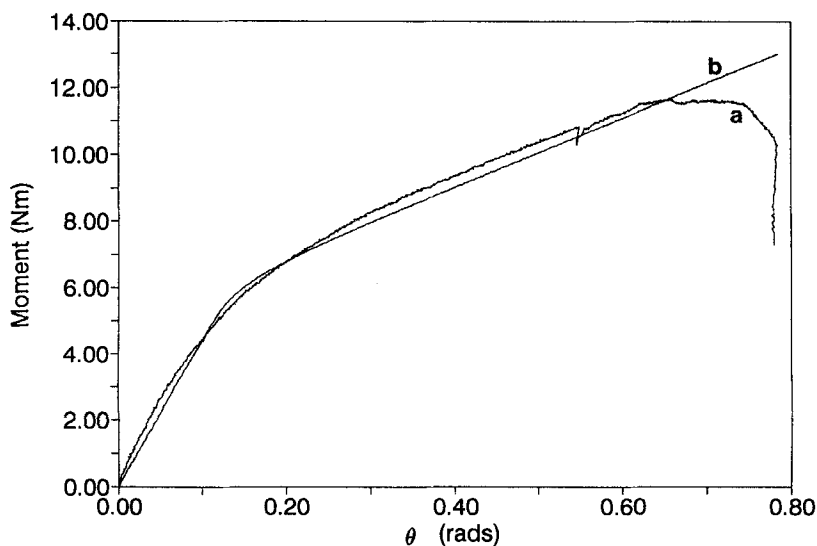


FIGURE 4 Applied couple, M , vs. joint rotation, θ , for porous metal joint. (a) Experimental curve (cf. Figure 1), (b) theoretical curve from equations (10) and (12).

and it can be seen that the initial part of the experimental curve, corresponding to $\theta < \theta_c$, is slightly concave towards the abscissa although, from the model, we should expect linear behaviour. Using equations (10) and (12), it is found that the shear modulus of the polymer, G , is 11.2 MPa and the effective modulus, \tilde{G} , equal to 2.6 MPa. Using equation (5), a value of 3.7 mm for e , and taking the surface fraction of fibrils, f , to be *ca.* 20% (a value estimated from porosity figures and visual observation of fracture surfaces), we obtain a value of t of *ca.* 0.6 mm. This value should be halved, approximately, in order to estimate the separation between the bulk polymer and the metal substrate for each metal/polymer interface. A value of 0.3 mm would seem a little high but, nevertheless, compatible with observations of partially fractured joints. A value of *ca.* 0.11 has been obtained for θ_c , corresponding to *ca.* 0.3 for γ_c . These figures seem to be in reasonable agreement with equivalent values of θ and γ_{\max} at the onset of failure in dense metal joints, thus corroborating the model. In the latter case, when the bulk polymer/metal interface starts to separate at $r = r_e$, this should correspond to the onset of catastrophic failure since no anchored polymer is present to produce fibrils restraining overall polymer/metal separation.

From Figure 4 we may estimate the final failure stress of the fibrils, by assuming that fracture occurs more or less catastrophically when the maximum value of couple, M , has been obtained. Taking the joint to be in its fibrillar state down to a very small radius, r_p , (*i.e.* virtually homogeneous) the maximum shear stress at $r = r_e$, τ_{\max} , is given by:

$$\tau_{\max} = \frac{2M}{\pi r_e^3} \quad (13)$$

assuming continuous polymer at the interface. However, the actual stress will be nearer to:

$$\tau_{\max} \approx \frac{2M}{\pi r_e^3 f} \quad (14)$$

allowing for the surface fraction of fibrils. Taking M to be *ca.* 11 Nm, we obtain a value of τ_{\max} of *ca.* 35 MPa, which is in satisfactory agreement with values for the ultimate strength of such polyurethane materials.

CONCLUSIONS

A study of adhesion to porous substrates has been undertaken. By testing cylindrical, torsional joints consisting of stainless steel adherends, both dense and sintered, bonded with a polyurethane "adhesive", it has been shown that the effective energy of adhesion can be an order of magnitude greater with a porous substrate. This effect has been attributed to mechanical adhesion, or the anchoring of polymer in interstices within the substrates. After initial polymer/metal interfacial adhesion has failed, polyurethane is drawn out of interstices and gives the necessary mechanical support so that the system remains intact. The "glueline" has been modelled as a

“composite” interface in shear and satisfactory agreement obtained with experimentally observed behaviour.

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