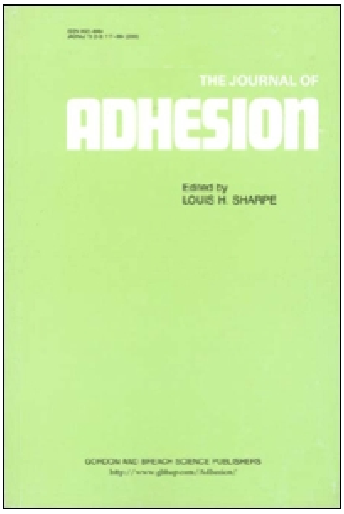
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

The Variation of Bond Strength with Temperature: A Preliminary Study of Metal-to-Metal Adhesion

H. Foulkes; J. Shields; W. C. Wake

To cite this Article Foulkes, H. , Shields, J. and Wake, W. C.(1970) 'The Variation of Bond Strength with Temperature: A Preliminary Study of Metal-to-Metal Adhesion', The Journal of Adhesion, 2: 4, 254 — 269

To link to this Article: DOI: 10.1080/0021846708544599

URL: http://dx.doi.org/10.1080/0021846708544599

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The Variation of Bond Strength with Temperature: A Preliminary Study of Metal-to-Metal Adhesion

The late H. Foulkes*, J. Shields† and W. C. Wake*‡

**Rubber and Plastics Research Association of Great Britain*
Shawbury, Shrewsbury, Salop, England.
†British Scientific Instrument Research Association
South Hill, Chistlehurst, Kent, England.
‡Now at The City University, London, E.C.1. England.

(Received July 10, 1970)

ABSTRACT

Experiments have been made with a torsional shear apparatus with aluminium, stainless steel and titanium alloy substrates. The bond strength measurements are independent of joint area, only slightly affected by thickness and appropriate conversions from torque to stress are discussed. At low temperatures, failure is by brittle fracture within the adhesive; at higher temperatures the adhesive behaves in a ductile manner and areas of substrate are left clean. The site of failure is discussed and evidence suggests that a layer of adsorbed liquid from the cleaning process might provide the weak layer initiating failure.

INTRODUCTION

IN THE SEARCH for improved high temperature metal-to-metal adhesives there are two fairly well defined and separated aspects. There is the need to obtain polymers that are inherently resistant to high temperatures and there is a need to understand the physical processes whereby bond strength decreases with increasing temperature. Thermal stability implies not only freedom from degradation in the presence and absence of air, but also the maintenance of adequate physical properties characteristic of thermosetting and not of thermoplastic polymers. However, even thermosetting resins that have no softening point do show a fall in adhesion as temperature rises quite independent of any decomposition process. It is the purpose of this paper to discuss the phenomena and to show that with this fall is associated changes in the nature of the failure process.

In the present study proprietary adhesives have been used as models for a high temperature adhesive as the maximum temperature at which they can be used and the somewhat higher temperature at which load bearing is negligible are more easily realised experimentally.

The measurement of bond strength used was the torsional shear determined with a "napkin ring" test piece sheared in the RAPRA-Wallace Napkin Ring Shear Test Instrument[1,2].

J. ADHESION, Vol. 2 (October 1970), p. 254

EXPERIMENTAL

Method of Making Test Pieces

There are several methods of test piece manufacture, two of which, centre pin and RAPRA jig assembly, are described by Humpidge and Taylor[1].

The essential feature of all methods is to obtain good alignment of the two halves of the joint as with a glue-line thickness of 0.001 in, a very small degree of non parallelism can lead to an appreciable reduction in measured strength due to stresses other than pure shear developing in the joint under a torsional load.

If thick joints are required wire spacers are used which consist of short lengths, 0.1 in, of wire of the appropriate diameter. Normally four spacers are used, placed on a circle in the centre of the annulus. This annular placement differs from the radial direction of the spacers used by Bryant and Dukes.[3]

The flow pattern of a film adhesive during joint formation has been studied by bonding one annulus to a sheet of plate glass and using time-lapse photography. A selection of the frames can be seen in sequence in Figure 1. Flow of the adhesive is in a radial direction leading to the distinct flow lines referred to in a later section.

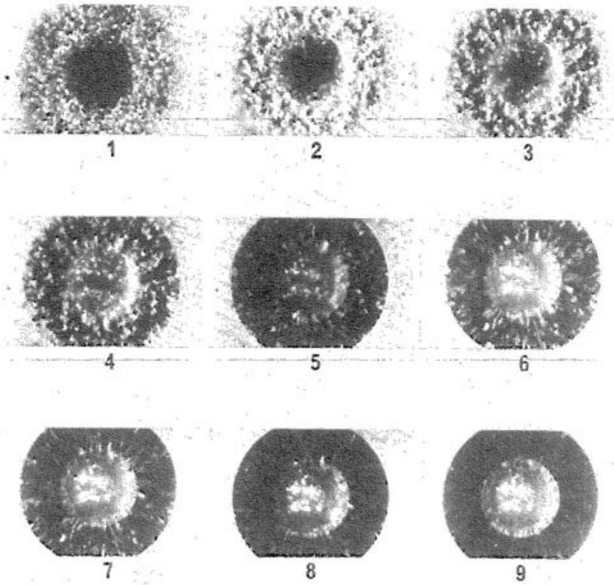


Figure 1. Time-lapse Photographs Showing Flow of Adhesive (Redux 775) During Formation of Bond.

MEASUREMENT AND CALCULATION OF TORSIONAL SHEAR

The use of the napkin ring test piece was proposed by de Bruyne[4] in 1951 and was first used in research on adhesion by Gillespie and Rideal[5]. It has been examined in detail with a discussion of the effects of a number of variables[3] and comparisons have been published of the napkin ring with circular butt joints in tension, torsional shear and simple shear[6]. These references have established that the measured stress at failure is independent of the dimensions of the test piece and that, unlike the simple or double lap shear test piece, it is possible to regard the failure as a true shear uncomplicated by a cleavage or peeling stress which invariably initiates the failure process in a lap joint.

It is important to avoid the existence of cleavage or peeling stresses when investigating the effect of temperature on the joint. These unwanted stresses arise from the lack of symmetry in a simple lap joint together with the difference in the rigidity of adhesive and adherend. With the use of a torsional shear the relative rigidity of adhesive and adherend is not important to the measurement of failure stress though it adds difficulties to the measurement of failure strain if this is required. Figure 2 shows the type of napkin ring test piece, a range of test pieces being used having different dimensions for r_1 and r_2, the outer and inner radii respectively. The calculation of stress in the plane of the adhesive has been given variously and it is necessary to discuss its derivation from the measured torque, T.

Bryant and Dukes[3] quote the required relation as $S_o = \frac{2r_1 T}{\pi(r_1^4 - r_2^4)}$ where S_o is the stress at the outer radius (r_1), where it is maximal and the adhesive behaves elastically. If $r_1 \simeq r_2$, i.e. the radius is large compared with the thickness of the wall of the napkin ring, this reduces to the expression given by de Bruyne and quoted with a certain reservation by Sneddon,[7] *viz.*,

$$S = \frac{T}{2\pi(r_1 - r_2)R^2} \text{ where } R = \text{mean radius}$$

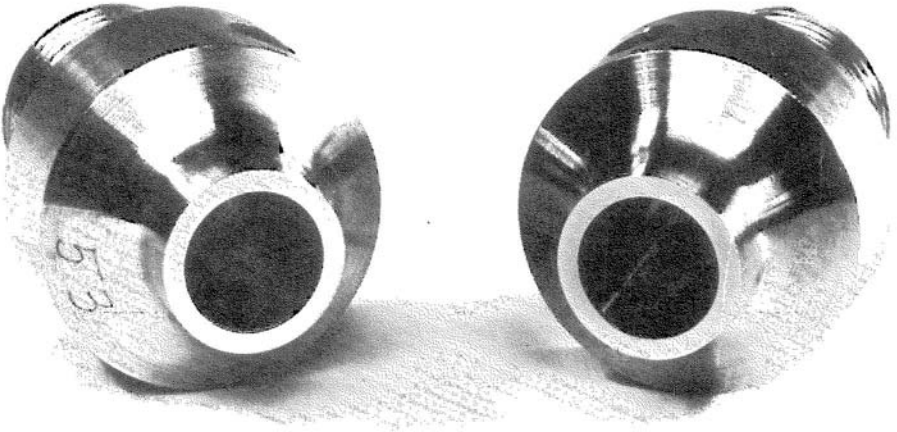


Figure 2. Napkin Ring Test Pieces.

Bryant and Dukes have shown the first of these relations to give bond strengths independent of variation of r_1 and r_2 when used with an elastic adhesive. The adhesive used was a silicone rubber giving a rather low bond strength (140 psi) but, as for all rubbers, exhibiting linear elasticity in shear.

The use of one of these relations assumes perfect elasticity to the point of failure. However, as the present investigation progressed it became apparent that the adhesive most frequently showed clear indication of ductile failure. If it is assumed that the bond fails not by brittle failure of the adhesive nor by a form of interfacial failure corresponding to brittle failure but that failure occurs when the adhesive is in a ductile condition, then the stress across the adhesive annulus will be uniform and $S = \frac{3T}{2\pi(r_1^3 - r_2^3)}$ a result obtained by Nadai[8]. Additionally, under these conditions, the result recorded by the test equipment will be sensitive to the rate of strain. If ductile failure becomes possible as the temperature increases then a condition may be imagined in which torque is applied up to the yield stress and is then held constant. Under elastic conditions the stress is greater on the outer circumference and plastic yield will therefore first occur here and, with slight increase in torque the elastic/plastic boundary will move across the annular thickness until the fully plastic state is obtained. Under the test conditions used, the torque increases at a uniform rate and equilibrium conditions never occur. If S_y is the yield stress of the adhesive, continuous plastic deformation will occur when $T > 2S_y \pi (r_1^3 - r_2^3)/3$ and there will be accelerating flow under a torque of $T - 2/3 \{S_y \pi (r_1^3 - r_2^3)\}$, until the maximum strain is exceeded. Depending on the extensibility of the adhesive at the temperature, so will the recorded torque at failure exceed the yield stress. It will also be very dependent on strain rate. Insofar as failure occurs when the adhesive is in a plastic state, the test procedure will overestimate the equilibrium strength of the joint, and this overestimation will be greater as the temperature increases once yield is occurring. The results showing a temperature/joint-strength profile that are reported in a later section necessarily exhibit this error at higher temperatures.

Influence of Dimension of Test Piece on Results

The foregoing discussion makes it important to consider again the question of whether napkin ring test results are independent of the test piece dimensions. Table 1 shows failing torques recorded using Redux 775 at room temperature with 14 different aluminium test pieces and the results are arranged in order of increasing interfacial surface area from 0.032 to 0.245 sq. in. The test pieces were made in several different batches, the forming jig holding 6 of different sizes at one time.

Table 1. Failing Torques for Various Annular Dimensions.

Outside Radius	*Inside Radius*	*FAILING TORQUE, LBS-IN.*									
IN.	*IN.*	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
.16	.125	50	53	51							
.25	.211	144	151	157	120	141					
.19	.125	113	104	116	109	112	111	114			
.325	.291	237	225	224	235	228					
.2905	.25	193	211	210	188	213					
.25	.188	229	238	236	226	229	220	204			
.2105	.125	161	170	178	172						
.625	.6	626	582								
.375	.3225	433	441	442	412	415	333	347			
.325	.25	491	484	452	435	366	448	422			
.25	.125	315	304	300	316	316	311	295	319	320	306
.375	.291	661	722	650	600	647	577				
.35	.25	657	565	574	602	546					
.375	.25	787	825	790	794	728	807	781			

A total of 80 bonds were broken as recorded in Table 1 and the measured torque plotted against the appropriate function for elastic deformation in Figure 2 and plastic deformation in Figure 4. The best estimates of the breaking stress are given by the slope of the line fitted by least squares.

For elastic failure; $$\text{Torque} = 11{,}550\,\frac{(r_1{}^4 - r_2{}^4)}{2r_1} + 17.5$$

For plastic failure; $$\text{Torque} = 10{,}140\,{}^{2}\,\frac{2(r_1{}^3 - r_2{}^3)}{3} + 18.8$$

The mean failing torques for each size of test piece are plotted as the points on Figures 3 and 4 and the scatter shown by the vertical lines. The fit of the two lines can be judged from the calculated sum of chi squared values for these points and the lines, 24.5 for those calculated assuming the elastic equation and 9.6 (both with 12 degrees of freedom) with the plastic equation. It is noteworthy that the most deviant point on Figure 3, which refers to the test piece of largest radius (0.625 in) and thinnest wall (0.600 internal radius), lies well on the line when the plastic equation is used.

The calculated breaking stresses are 11,550 psi with the elastic equation and 10,140 psi with the plastic equation, a drop of 14%. It seems reasonable to use the equation appropriate to the mode of failure but it happens that with the particular adhesive used in these experiments the mode of failure is

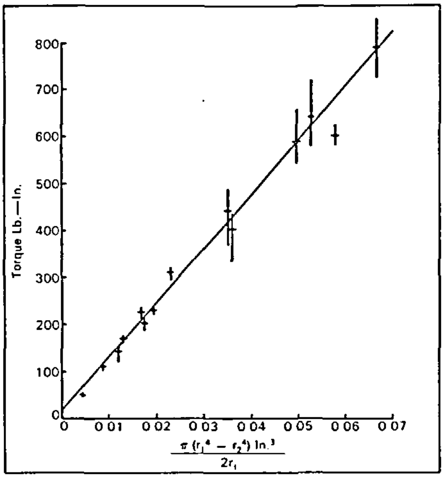


Figure 3. Breaking Torque of Napkin Ring as Elastic Function.

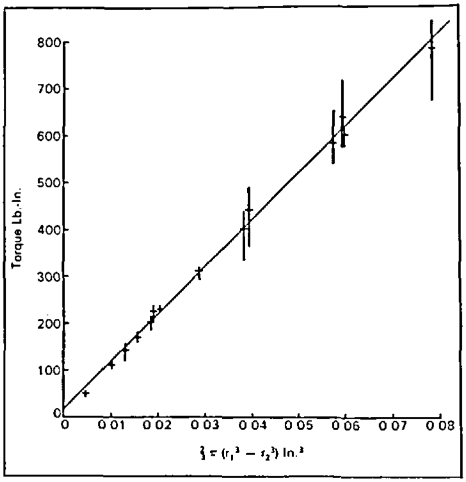


Figure 4. Breaking Torque of Napkin Ring as Plastic Function.

uncertain being at room temperature in the transition region between low temperature brittle failure and definitely ductile failure at slightly elevated temperatures. On balance the plastic equation will be used at room temperature and the residual variance of torque about the regression line when the plastic equation is used gives a standard deviation for a single observation of 30.2 lb.-in. However, there is some indication that the scatter of the results increases with increasing value of torque and this figure may exaggerate the variability to be expected with the size of test piece used for the temperature profile quoted later in this paper. This residual variance of the torque would give a coefficient of variation on the test piece of 0.25 - 0.125 in radii of 10% compared with 3% calculated from the spread observed at this particular size of test piece. It is therefore the latter figure of 3% which is appropriate for results given later.

Whichever equation is used it seems certain that, as expected, the result obtained is independent of the dimensions of the napkin ring, although test pieces requiring high torque seem to give more scatter, possibly due to defects in the prototype machine when used at a torque level in excess of the design level.

Influence of Thickness of Glue Line

The effect of thickness of the adhesive layer on joint strength has been discussed by a number of authors[9] and Bryant and Dukes[3] summed up the information about napkin ring shear test pieces then available. Briefly, they confirm that an effect exists in the usual sense of 'the thinner the joint, the stronger the bond', that the effect is of smaller magnitude with napkin ring shear than with lap joints and that sensitivity is slightly greater when the annulus is wider. In a later publication[6] they attribute part at least of the effect to a change in the rate of straining which occurs with increased thickness if the rate of twist of the metal parts is kept constant.

Results obtained in the present investigation are shown in Figure 5 and refer to an epoxy adhesive, Araldite AT1 with aluminium test pieces. They are plotted double-log in the manner employed by Bryant and Dukes[3,6] and show the expected linearity with perhaps some deviation at the lower end of the thickness range. A two fold variation in thickness produces less than 10% change in breaking strength. Experience shows that with unsupported adhesives gluelines of about 0.001 in. are obtained. If thicker gluelines are required spacers are used. Contrary to some opinions we have not found spacers to interfere with the level of adhesion recorded as is apparent from Figure 5.

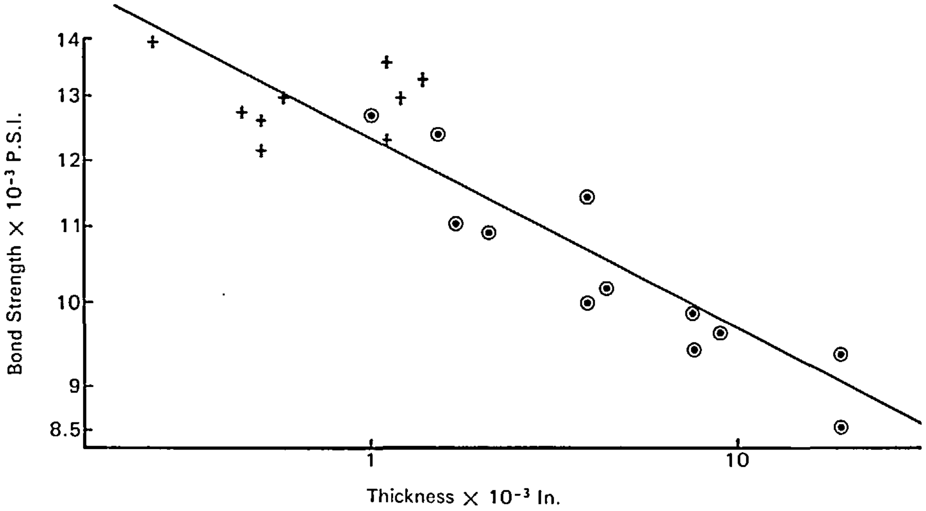


Figure 5. Effect of Glue-line Thickness; + without spacers; ○ with wire spacers set wholly within adhesive.

Rate of Straining

The work of Bryant and Dukes demands that for absolute determination of bond strength, the rate of straining as well as the temperature and thickness of the test pieces should be controlled. This was not possible with the apparatus used and it must be accepted that the temperature profile quoted has superimposed on the temperature change a rate of deformation change. As the temperature increases the modulus falls and the imposed rate of straining remains closer to that implied by the constant speed of the motor. At low temperatures and therefore higher stresses, deformation of the wire through which the load is transmitted to the torque wheel will be added to a possible slowing of the motor and hence a reduction in the rate of strain. The actual strain at the moment of fracture has not been measured in this work but will be greater as the temperature increases.

THE NATURE AND SITE OF BOND FAILURE

There have been numerous references in the literature to arguments based on thermodynamics, stress concentration or crack propagation which purport to show that failure of a bond is necessarily a cohesive failure of substrate or adhesive; usually the latter because it is weaker. Most of this discussion assumes a brittle fracture mechanism by crack initiation and propagation. However, laboratory workers have long distinguished adhesive from cohesive failure and tacitly assumed that the apparently clean substrate obtained after adhesive failure of a bond contains invisible adhesive failure being thought to occur a few molecules away from the interface. Voyutskii and his colleagues[10] have attempted to demonstrate this by synthesizing polypropylene containing C^{14} and measuring the radiation intensity from the substrate surface after peeling away the labelled polypropylene. On a polypropylene substrate, as would expected from the diffusion theory of autohesion, the radiation intensity increased with time of contact before separation. The same, however, applied when glass was used as a substrate. For unoxidised and oxidised copper the material left after peeling is scarcely more than would be accounted for by minor irregularities of the surface or occurring in the peeling process. Huntsberger[11] has offered evidence based on interferometry that polyisobutene peels cleanly from an alkyd resin substrate with a mean change in thickness of -1.3 ± 3.3 Å.

The argument put forward by one of us some years ago[12] pointed out that the most probable site for cracks likely to grow and hence initiate failure is at the interface and that failure would necessarily propagate into the resin phase. This implies failure by a brittle mode and at low temperatures this appears to be true. Examination of test pieces broken at low temperatures suggests brittle fracture although movement of the two surfaces against each other after failure has occurred obscures the exact nature of the broken surfaces. There is no doubt, however, that it is almost wholly within the resin. Even failure by a species of brittle mode, that is a failure initiated and sustained by crack growth, can be interfacial, though under special circumstances[13].

At room temperature, however, many adhesives fail by a ductile mode and, as is indicated elsewhere in this paper, this is true for the Redux resin used in this investigation. Ductile failure results in adhesive remaining stuck to one face of but not both at any particular site; the bare areas of metal on one of the broken test pieces match the areas of adhesive on the other test piece. This is apparent from Figure 6, a photograph of a Redux bond but typical also of other adhesives. Examination of the apparently clear areas of this broken test piece by replication of the surface with polyvinylalcohol failed to show detail other than that of the original metal surface. However, on one occasion over a small area some residue of the adhesive was found, and this is reproduced in Figure 7.

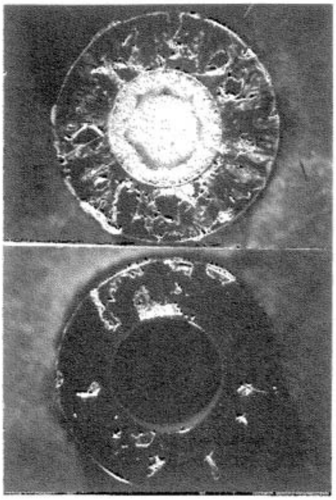


Figure 6. Typical Ductile Failure of Redux 775 at Room Temperature.

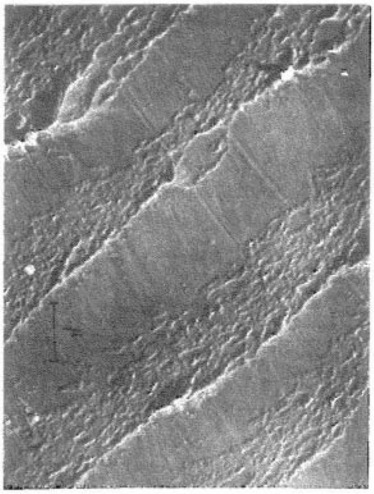


Figure 7. Electron Micrograph of Surface after breaking of Joint. Adhesive; Redux 775.

The adhesive occurs in broad bands across this picture. They are spaced at about 3–4 μm intervals and apparently reproduce the flow pattern discussed previously though here on a very much smaller scale. It must be emphasized that although these features have been found they are rare and, as far as the electron microscope can study the surface, it is mainly featureless.

Ellipsometry

Reference has already been made to Huntsberger's use of interferometry. We were fortunate in having ellipsometry available to examine the surface of metal exposed by fracture of the joint in an endeavour to identify films of materials on the apparently clear surface left after adhesion failure of napkin ring test pieces. As is well-known, plane-polarised light is elliptically polarised on reflection from a polished metal surface. From the orientation of the ellipse it is possible to calculate optical constants for the reflecting surface and any transparent film thereon.

The technique was used on stainless steel napkin ring bonding surfaces which had been prepared by polishing through the following sequence:

a) machine honed, lapped flat and polished with alumina (particle size 0.025 μm) in methanol on a glass plate,
b) cleaned with paper tissue soaked in trichloroethylene,
c) washed in trichloroethylene.
d) rinsed in acetone and dried in warm air from a drying fan.

Optical parameters were determined for the freshly prepared steel surface, similar surfaces immediately after breaking an adhesive bond and surfaces of the steel test pieces which had been heated at the curing temperature of the adhesive. The adhesive was a fluoroalkylenated aromatic polyimide[14]. The surfaces were examined in an ellipsometer[15] and the orientation of the reflection ellipse and the ratio of the principal axes determined[16]. Following usual practice, Figure 8 plots the angle between the plane of incidence and the major axis χ against γ, where $\tan \gamma$ is the ratio of minor to major axis. The observed data are shown as individual points; the full lines are those expected for an oxide film on steel (calculated from the refractive index of the actual film present on the freshly prepared, unbonded test piece), and a film of the adhesive. The observed values lie closer to the curve computed for oxide films on steel and, after the bond has been broken, the evidence suggests that only an oxide layer exists the thickness of which is influenced by the temperature at which the test piece has been held and broken.

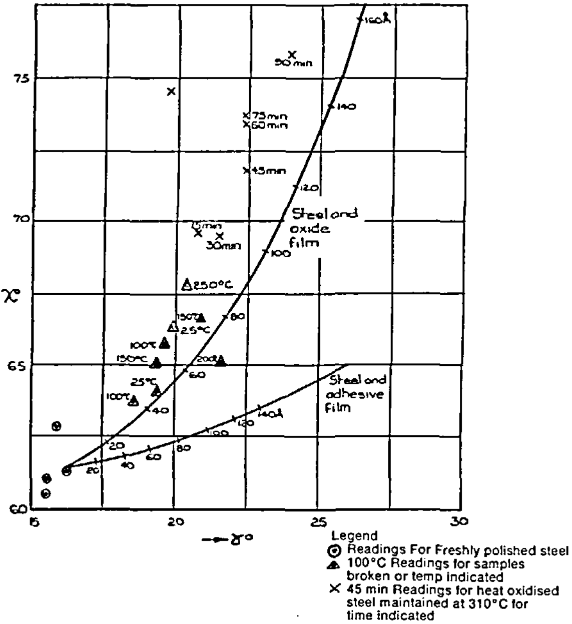


Figure 8. Variation of Parameters of Elliptically Polarised Light Reflected by Steel.

Influence of Nature of Substrate

A series of bonds were made with Redux adhesive with test pieces of aluminium, stainless steel and titanium alloy. The test pieces were all lapped flat on a surface plate and wiped clean with chloroform. The alloys used were: Aluminium, BSL65; Stainless Steel, FV520B; Titanium, IMI205.

The adhesive was used in the form of thin (.025″) sheet which was placed between the test pieces, loaded into the curing jig and cured 6 at one time for $1/2$ hr. at 150° C. Testing was over a wide range of temperature and test pieces were chosen randomly for breaking at any given temperature. The results are plotted in Figure 9 calculated on the basis of the elastic equation at low temperatures, plastic equation at high temperatures and overlapping is the intermediate zone. It shows clearly that the breaking strength is a function of

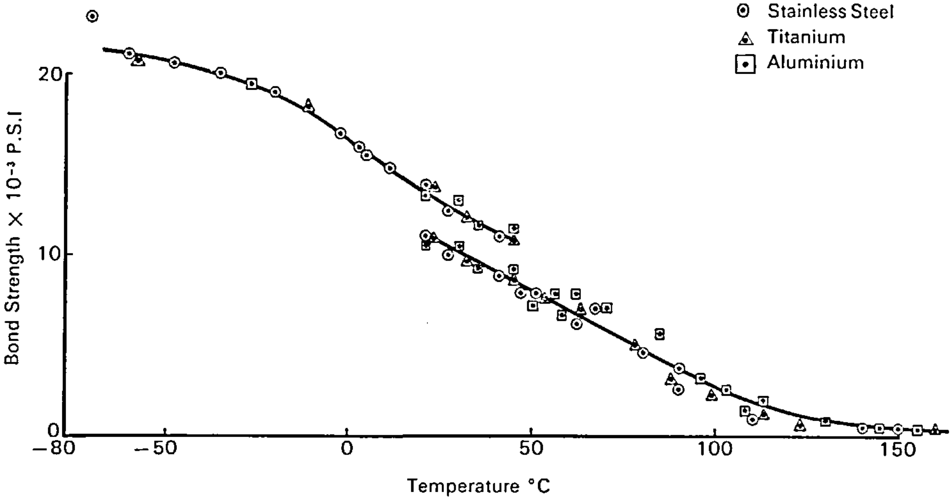


Figure 9. Bond Strength vs Temperature for Redux 775 on Three Substrates. Upper curve, stress calculated as elastic; lower curve, stress calculated as plastic.

temperature independent of substrate and suggests that throughout the temperature range it is the bulk properties of the adhesive which determine the bond strength. The appearance of the broken bond alters with temperature. Figure 10 shows the test pieces formed with highly polished adherends and broken at −196° C; the failure is cohesive and though the surfaces have been damaged by grinding together after fracture, the appearance is one of brittle failure. Figure 11 is of a test piece broken at −70° C; failure is mixed and there still appears substantial regions of cohesive failure. On photomicrographs at larger magnifications, boundaries between cohesive failure and adhesive failure are clearly visible. Figure 12 is a photograph of a test piece broken at room temperature; failure is adhesive apart from one small patch of cohesive failure. Bare patches of metal match exactly with those carrying

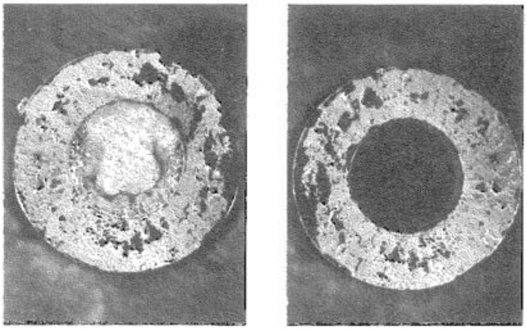


Figure 10. Test Pieces of Joint Broken at −196° C.

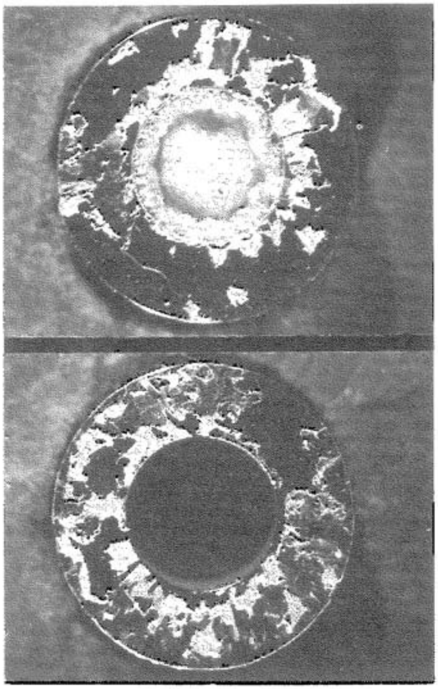


Figure 11. Test Pieces of Joint Broken at −70°C.

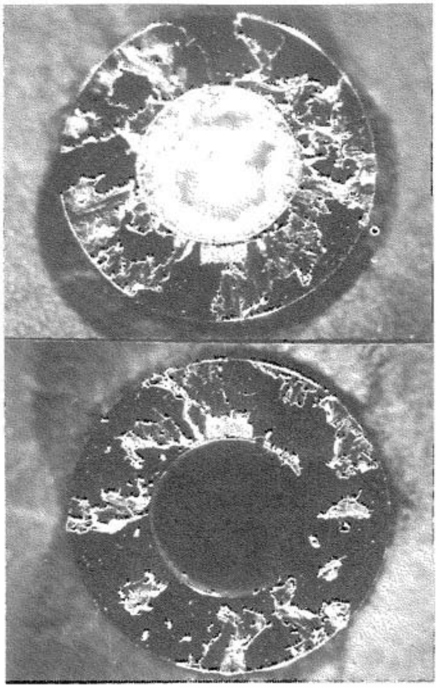


Figure 12. Test Pieces of Joint Broken at Room Temperature.

adhesive on the opposite adherend. Highly magnified images of the areas of adhesive failure show the edges of the patches of adhesive remaining on the metal to be free of the metal and to have been deformed in a ductile manner. It seems clear that *cohesive failure* with adhesive remaining on both adherends is a brittle failure and occurs at low temperatures. *Adhesive failure* occurs associated with ductile failure at higher temperatures. As would be expected, in the region brittle failure occurs, the bond strength is relatively insensitive to change of temperature whilst the marked decline in bond strength with rise of temperature is associated with adhesive failure and, apparently, with ductile behaviour of the adhesive.

Influence of Treatment of Substrate

As the electron microscope and ellipsometric studies were made with test pieces which had a much higher degree of surface finish than used in most of the bond strength determinations, a comparison of polished and unpolished adherends was made over a range of temperatures. Unpolished stainless steel test pieces were prepared by the standard lapping technique on a range of water-lubricated silicon carbide papers, wiped with chloroform, and gave a clean matt appearance. The polished test pieces for the comparison were similarly lapped but after this were polished on Metron B discs[17] impregnated with diamond paste finishing with $1\mu m$ diamond paste in a paraffin carrier.

The surfaces were then rinsed with detergent and washed for a prolonged time in distilled water. At this stage water broke clean over the surface but after drying with drying tissue the surface gave a contact angle of about 30° with water. The comparative results with Redux 775 film adhesive were:

Temperature of Test	*Joint Strength (psi)* Unpolished Surfaces	Polished Surfaces
–196°C	38,500	38,000
– 70°C	21,000	20,500
22°C	14,250	—
	14,350	13,800
62°C	8,000	9,600

After breaking the joints the contact angle of water was about 75° on apparently base metal where adhesive failure had occurred.

It is apparent that at low temperatures there is a barely significant tendency for slightly lower strengths with the polished surfaces but at 62°C unpolished surface gives a significantly weaker adhesive bond. Closer examination of the details of surface preparation revealed a situation where approximately the same standard of finish arrived at by different routes, gave substantially the same bond strength. The approximate contact angle shown by water on the adherend surface before and after making and breaking a bond under conditions to give adhesive failure varied significantly with the surface preparation. The salient points are made in Table 2.

Table 2. Effect Of Final Stage of Surface Preparation on Contact Angle and Bond Strength

Polished With 1μm Diamond Paste in Organic Media

Nature of Treatment	*Detergent Water Tissue*	*Heated 90°C in Pyroclean Washed in water*	*Washed in chloroform and wiped*	*Washed in carbon tetrachloride*
Contact angle of water on surface before bonding	30°	0°	60° 70°	60° 70°
Bond Strength	14,250 14,350	13,700 13,800 13,800 14,500	15,350	13,900 14,300
Contact angle of water on surface after bonding	75°	10-15°	75°	75°

Attempted Radiochemical Examination of Surface

The obvious conclusion from the independence of bond strength and contact angle of water on the finished surface is that wiping or other treatment with chloroform or carbon tetrachloride leaves a layer of the solvent unaffected by drying and which provides the parting surface when ductile failure occurs. An attempt was made to detect this layer by using C^{14} labelled carbon tetrachloride. One-tenth mC. of C^{14} carbon tetrachloride was dissolved in 5 ml of Analar grade carbon tetrachloride and used to wipe the surfaces of the prepared adherends in the standard way. Some of the adherends were placed directly onto X-ray sensitive film and others were used to make test pieces which were broken to give adhesive failure and the surfaces, after photography were also placed on X-ray film. No images were obtained as the X-ray film developed after 8 days exposure. Calculation from the known sensitivity of the film and the activity of the labelled carbon tetrachloride shows that a faint image would be expected from a layer 10 molecules thick and a strong image from 100 molecules layer. The detection means used in the Russian work cited[10] was, in fact, much more sensitive than X-ray film, and, even so, some of their results were of doubtful significance.

DISCUSSION

The determination of bond strength over a range of temperature in the torsional shear apparatus involves an examination of the broken test piece to decide whether to calculate the shear strength with the aid of the 'elastic' or the 'plastic' equation. The elastic regime holds at lower temperatures and the failure is by brittle fracture in the bulk of the adhesive. Under these conditions the change in bond strength with temperature is small and although evidence is not presented here, it is obvious that a rigid material with high transition temperatures is advantageous if freedom from temperature effects is desired. If the yield stress is less than the stress value at which it would undergo brittle shear, then failure will be in the ductile mode. The stress in the napkin ring test piece will be biaxial as cooling or cross-linking stresses will add a second radial component inward from both faces and zero at the centre line of the annulus as well as adding to the first component by a circumferential stress. This radial component will lower the applied stress for initiation of plastic flow from that which obtains in unaxial stressing. There need be no surprise therefore that apparently brittle materials fail in adhesive bonds by a ductile mechanism and where this is so, the recorded bond strength will decrease with increasing temperature but will also be rate dependent. In the absence of experimental data related to known and constant rates of straining, there must be some degree of arbitrariness about the temperature/strength profile particularly at temperatures much above the point where ductile behaviour becomes apparent.

Many adhesives are mixtures of polymers and at elevated temperatures it is the ductile component which determines the mode of failure. It is unlikely that organic polymers will be available as metal adhesives with T_g above the temperatures of operation now being considered (400-500°C) so that some fall of properties from those at room temperature seem inevitable. More work is therefore needed on the ductile mode of failure of adhesives as distinct from the brittle mode. In particular, the mechanism whereby ductile failure is associated with clean removal of adhesive from the substrate, albeit randomly in patches, is obscure. The present work has shown clearly that true adhesive failure does occur under these conditions without failure in the substrate or failure in the adhesive leaving films of molecular dimensions. Instead, the possibility of failure within or parting at an absorbed layer of molecular dimensions exists. This is, of course, a form of the Bikerman weak layer theory and even in the present form the suggestion is not new although it is difficult to identify its earlier explicit formulation[18].

It is also clear that the main contribution to the fall in strength with increasing temperature over the range where this occurs markedly, is a plastic flow phenomenon.

ACKNOWLEDGMENT

This paper records work carried out with a research grant from the Ministry of Technology U.K. (Directorate of Materials) and the authors' thanks are due for permission to publish. Most of the experimental work reported was carried out by Henry Foulkes and his colleagues recall with sadness the loss by early death of Henry and his wife Irena on Christmas Eve 1969.

NOMENCLATURE

r_1, r_2	Inner and outer radii, respectively, of napkin ring test piece.
S	Stress in plane of adhesive when this can be regarded as approximately uniform.
S_o	Stress in plane of adhesive at outer radius of test piece when stress is not uniform.
S_y	Yield stress of adhesive.
T	Breaking torque.
γ	Tan γ is the ratio of the major to minor axis of the reflection ellipse.
χ	Angle between plane of incident light and the major axis of the reflection ellipse.

REFERENCES

1. R. T. Humpidge and B. J. Taylor. *J. Sci. Instr.* 44, 457 (1967)
2. H. W. Wallace and Co. Ltd., *Torsional Shear Adhesive Test Apparatus,* (1969).
3. R. W. Bryant and W. A. Dukes, *Brit. J. Appl. Phys.* **16,** 101 (1965).
4. N. A. deBruyne, in "Adhesion and Adhesives", Eds. N. A. deBruyne and R. Houwink, Elsevier, Amsterdam (1951)
5. J. Gillespie and E. K. Rideal, *J. Coll. Sci.* **11,** 732 (1956).
6. R. W. Bryant and W. A. Dukes, S.A.E. Aeronautic and Space Eng. and Mfg. Meeting, Los Angeles, (Ref. 670855), (1967).
7. I. N. Sneddon, in "Adhesion", Ed. D. D. Eley, Clarendon Press, Oxford (1961).
8. A. Nadai, "Plasticity: A Mechanics of the Plastic State of Matter", McGraw Hill, New York (1931).
9. W. C. Wake, *Trans. Inst. Rubber Ind.* **35,** 145 (1959).
10. V. K. Gromov, M. B. Neiman, V. L. Vakula and S. S. Voyutskii, *Russian J. Phys. Chem.* **37,** (9), 1125 (1963).
11. J. R. Huntsberger, *J. Polym. Sci.* **A1,** 1339 (1963).
12. W. C. Wake, in "Adhesion", Ed. D. D. Eley, Clarendon Press, Oxford (1961).
13. R. L. Patrick, J. A. Brown, L. E. Verhoeven, E. J. Ripling and S. Mostovoy, *J. Adhesion* **1,** 136 (1969).
14. J. P. Critchley, V. C. R. McLoughlin, J. Thrower, I. M. White, *Chemistry and Industry,* **(28),** 934 (1969).
15. Gaetner Scientific Corporation, "Ellipsometers".
16. National Bureau of Standards of the U.S. *Ellipsometry in the Measurement of Surfaces and Their Films,* Misc. Publ., 256, Washington (1964).
17. Metron B Discs, Metallurgical Services, Ltd., Betchworth, Surrey.
18. W. G. Campbell, *Adhesion and Adhesives, Fundamentals and Practice,* Soc. Chem. Ind., London (1954).