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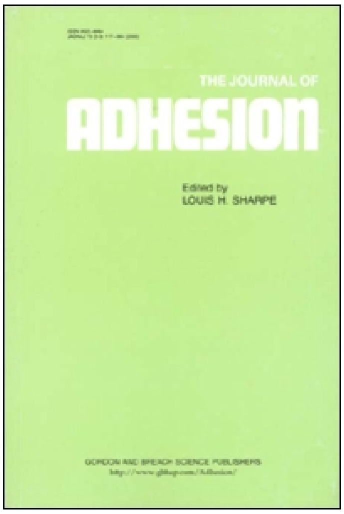

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THE EFFECT OF MOISTURE ON THE STRENGTH OF STEEL-STEEL CYANOACRYLATE ADHESIVE BONDS.

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ABSTRACT

The effect of humid ageing on the bond strength of steel-steel cyanoacrylate bonds has been investigated. Such systems rapidly lose most of their bondstrength while under similar conditions polycarbonate-polycarbonate bonds remain virtually unaffected. This loss of strength can be attributed to the formation of an oxide layer at the substrate - adhesive interface and the simultaneous surface hydrolysis of the polymer. It has also been shown that the adhesive itself is relatively impermeable to water and that the most likely method of ingress into the bond would be via a "wicking" mechanism along the substrate/polymer interface.

INTRODUCTION

One of the major problems of adhesives ingeneral and adhesives based on polycyanoacrylates in particular is their poor moisture resistance. Earlier work[1] has shown that the moisture resistance of metal-metal cyanoacrylate bonds is poor whilst bonds of this adhesive with plastics or rubbers show excellent resistance to moisture. A good deal of work has been published[2,3,4] and a considerable wealth of data accumulated on the effect of moisture on the adhesive strength of structural adhesives yet the

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mechanisms involved in the failure of the adhints is not clearly understood. Falconer et al.[5] examined the response of epoxy adhesive joints to conditions of high humidity and suggested the existence of materials at the interface which were more sensitive to water than the main bulk of the polymer. Evidence for this conclusion was provided by the work of Orman and Kerr[6]. These workers proposed that water was adsorbed at the metal or more likely at the metallic oxide surface. The rate of movement of water over such surfaces is extremely rapid and would be expected to be much faster than simple diffusion through the bulk polymer. Once the water reaches the interface it is thought to displace the adhesive from the surface via a so called "solubility parameter effect". Kwei[7], investigated two amine cured epoxy systems and explained the effect of moisture on the tensile strength of the polymer films in terms of the jump frequency of chain segments in the presence and absence of water. Mostovoy et al.[8,9], examined the stress-corrosion cracking of adhesively bonded aluminium specimens and concluded that water caused interfacial failure. Gledhill and Kinlock[10], adopted a thermodynamic approach and predicted that the work of adhesion would become unfavourably small in the presence of water. Brewis et al.[11], have shown that for epoxy systems, the adhesive strength is closely related to the amount of water adsorbed by the polymer. The vast majority of work carried out to date has been concerned with epoxy adhesives. The aim of the present paper is to explain why steel-steel cyanoacrylate bonds are so susceptible to heat and humidity.

EXPERIMENTAL

Materials

The adhesive, the main component of which is ethylcyanoacrylate was prepared and supplied by Loctite (Ireland Ltd. The lap shear specimens: Mild steel laps according to ASTM D1002-64 of dimensions 100 mm x 25 mm x 1.5 mm. Polycarbonate strips used were Makrolon (Bayer) of dimensions 300 mm x 25 mm x 3 mm. Glass laps were microscope slides of dimensions 76 mm x 26 mm x 1.1 mm.

Chemicals

Chromotropic acid (sodium salt) and sulphuric acid were Analar grade chemicals from B.D.H. Ltd. N,N-dimethylformamide was obtained from Hopkins and Williams Ltd.

All other chemicals were Analar grade reagents obtained from B.D.H. Ltd.

METHODS

Surface Treatment of Adherends

Mild steel laps were degreased in perchloroethylene and allowed to dry in a dust-free atmosphere. Polycarbonate strips were cleaned with a lint free tissue soaked in isopropanol.

Bond Preparation and Testing

Single lap shear joints were used throughout. Cyanoacrylate adhesive was applied to the surface of degreased laps, shim wires of specified dimensions were used to control thickness[12,13] and the bond was assembled to give an overlap of 125 mm. The joint was clamped together by two spring bonded clamps. The glue line thickness employed unless otherwise stated was 0.127 mm. All bond strengths were determined using an Instron Tensile Tester, Model 1102 at a rate of strain of 0.5 cm per minute. The lateral positions of the upper and lower grips were adjusted according to the thickness of the laps in order to minimise any possible peel effects.

Humid Ageing of Bonds

Accelerated hydrolytic degradation of the prepared bonds was carried out in plastic containers fitted with a perforated polystyrene false bottom, filled with water to a level below this false bottom. The bonds were placed upright in the chamber and the whole unit maintained at 50°C.

Determination of the Limiting Viscosity Number of Cured Adhesives

After breakage of the bonds the adhesive was carefully scraped off the substrate surface and dissolved in Tetrahydrofuran, (THF). The limiting viscosity number was determined using a suspended level viscometer at 30°C.

Hydrolytic Degradation of the Adhesive Polymer

Samples of polymer were obtained from broken lap joints dissolved in THF and precipitated with distilled water. The polymer was filtered, washed and dried at 40°C under vacuum. Samples of the cured adhesive (0.2 g) were placed in four glass stoppered conical flasks containing 50 ml of distilled water. Steel powder (2.0 g) was added to two of the flasks. The flasks and contents were maintained at 40°C for several days. The degree of degradation of the adhesive was monitored by the method of Leonard *et al.*[15] by colorimetrically analysing the formation of formaldehyde with chromotropic acid[14].

Preparation of Sandwiched Steel Bonds

Two mild steel laps were degreased and a drop of adhesive applied to one lap. The other lap was placed in contact with the adhesive and the two adherends rubbed together quickly once or twice. The laps were separated and the coating of adhesive allowed to cure completely at room temperature.

After curing, steel powder was dusted onto one cured surface (restricted to the central portion of the overlapping area). Adhesive was applied to the surface and the bond assembled using the other adhesive coated lap. The resulting adhint, which had a glue line of 0.24 mm was allowed to cure for 24 h at room temperature. This procedure was repeated to produce "thick" sandwich jointed with a glue line of 0.70 mm. These bonds were humidly aged, broken and the extent of oxide formation both on the substrate and the steel powder was assessed visually.

RESULTS AND DISCUSSION

The properties which make the alkylcyanoacrylate adhesives unique are their ability to polymerise rapidly at room temperature without the addition of a catalyst and to give a high bond strength between a wide variety of substrates within a few seconds or minutes. Despite these advantages the moisture resistance of cyanoacrylate/metal bonds is generally not good. On the other hand bonds with plastic show excellent resistance to moisture. This marked difference in behaviour is clearly shown in Fig. 1. The polycarbonate system remains virtually unaffected whilst the steel bonds loose approximately 90% of their strength. On visual examination it was found that for unaged bonds or after shorter times of exposure (up to 3 days) the mode of bond failure was essentially cohesive. After this period of time the failure changed from cohesive to adhesive. In addition there was a gradual growth of iron oxide at the interface as the humid ageing proceeded. The fracture surfaces after three and seven days resembled that of freshly degreased steel. Corrosion products were found after twenty one days of exposure to high humidity. The metal oxide was generated at the surface and there was no visible evidence to indicate that corrosion had commenced at the periphery of the bond and had progressed to the centre of the adhint.

Bond failure may be attributed to the adverse effect of moisture on the adhesive polymer. In order to assess the extent of degradation during humid ageing measurements were made of the limiting viscosity numbers for polymer samples in THF at 25^{o}C. The results are shown in Table 1. These results show an initial increase in molecular weight followed by a gradual decrease. The limiting viscosity number determined for a sample corresponding to a zero ageing time was obtained using material from a set of lap joints cured at room temperature for 24 h.

It is possible that during this time the adhesive will not be fully cured. Consequently the limiting viscosity number corresponds to a lower molecular weight than would be normally expected. During the humid ageing it would be expected that the adhesive polymerises and some degradation would occur at the same time. The values of $\{n\}$ reflect the net effect of these two processes. It can,

Figure 1. The Effect of Humidity on the Adhesion of Cyanoacrylate Adhesive to Mild Steel and Polycarbonate.

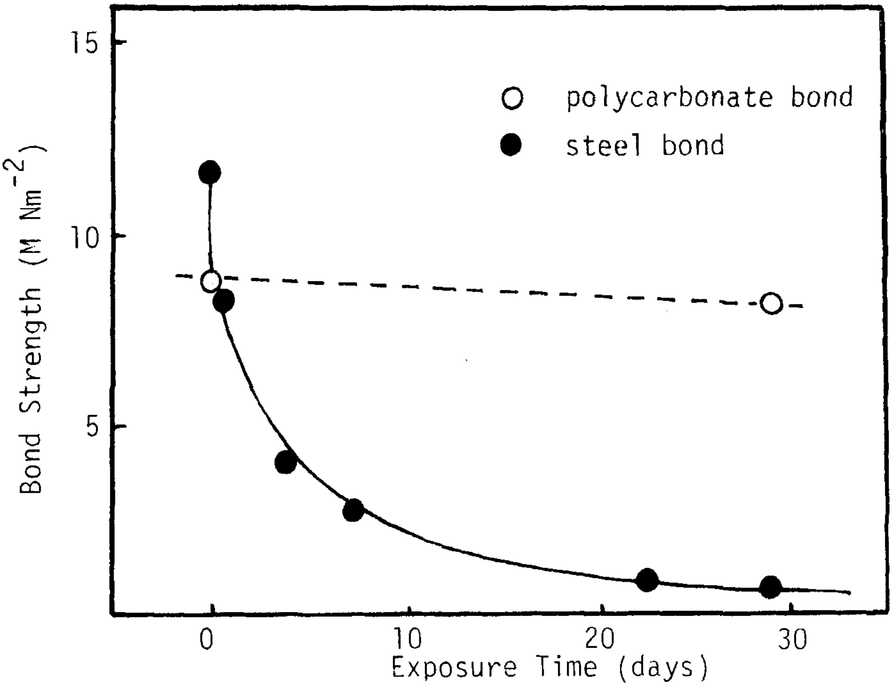

TABLE 1 The Effect of Humid Ageing on the Limiting Viscosity Number of an Alkylcyanoacrylate Adhesive in Tetrahydrofuran at 30°C.

{η}	Humid Ageing Time (Days)
0.51	0
0.55	3
0.61	7
0.57	21
0.58	28

however, be concluded that the catastrophic loss in bond strength cannot be explained solely in terms of hydrolytic degradation. The degradation of polyalkylcyanoacrylates is also accompanied by the production of formaldehyde[15]. The effect of the presence of steel on the decomposition of the adhesive can be illustrated by referring to the mass of formaldehyde produced after seven days of aqueous hydrolysis. The figures obtained were 625 and 1500 μg per g of polymer in the absence and presence of steel powder respectively. This clearly points to the catalytic effect of metal on the hydrolytic degradation of the cured adhesive. Given this to be the case then it might be expected that polymer hydrolysis would occur preferentially at the interface. This degradation in addition to the formation of a thick oxide layer would be expected to result in a massive loss in bond strength without significant changes in molecular weight of the adhesive. It would appear that bond failure is due to the condensation of water on the interface resulting in oxide formation and metal catalysed polymer hydrolysis. This picture of water induced bond failure would be more complete if the mode of penetration of water into the bond was known. In epoxide systems water has been shown to diffuse through the bulk adhesive[16-19] as opposed to "wicking" along the oxide/adhesive interface. Between the adhesive and the metal substrate there is an ever present layer of metal oxide. The bond has been subjected to a humid environment. Since corrosion products were found on the bonding surface, the interface would appear to be the destination of the water. There are two possible routes for water to reach the interface.

(1) Water vapour is adsorbed by the bulk adhesive through the periphery of the joint. The adsorbed water then diffuses through the adhesive layer and finally condenses at the interface.

(2) Water vapour enters directly through the interface at the oxide layer and thence to the interface.

Sandwiched steel bonds consisting of a thick layer of adhesive containing particles of steel powder were produced in order to investigate which of the two above routes was responsible for the penetration of water to the interface. After an appropriate time of exposure the degree of rusting of the steel powder and substrate surface could be assessed. There are several possible results.

Case (1) The adhesive is permeable to water vapour which can also penetrate through the oxide layer/adhesive interface. Rusting should occur on both the steel powder and the bonding surface.

Case (2) The adhesive is permeable to water vapour but water cannot penetrate through the oxide/adhesive interface. Rusting should initially occur on the sandwiched steel powder followed by oxide formation on the bonding surface of the steel substrate.

Case (3) The adhesive is not permeable to water vapour, and water can only enter through the oxide layer/adhesive interface. In this case corrosion should occur only on the bonding surface but not on the sandwiched steel powder.

Both thin and thick sandwiched bonds were made, the reason being that if water penetration proceeded by either case (1) or case (2) the sandwiched metal powder would suffer more rusting in the thick joints than the thin. The bonds were humidly aged for 14, 21, 28 and 42 days. A glass-glass sandwiched bond was also aged for purpose of control. It was found that the steel powder in the adhesive layer of the steel bonds remained bright and shiny even after 42 days. However, there was a gradual growth of iron oxide on the bonding surface as the humid ageing proceeded. In the case of the glass-glass bond no rusting of the steel powder could be detected. It was concluded that the adhesive is not permeable to water vapour and that water penetrates through the oxide layer/adhesive interface. This would suggest that case (3) is the mode of penetration of water into the joints. The transport of water appears to have been very rapid since within three days the mode of failure changed from cohesive to adhesive. The water that reaches the interface probably causes corrosion to the bonding surface of the substrate and degradation of the adhesive at the interface. The degraded adhesive forms a weak boundary layer which has poor mechanical strength. Water vapour diffuses through the interface and condenses onto the surface. This condensed water displaces some of the adhesive from the steel substrate and causes weakening of the adhesive between the substrate and the adhesive. This condensed water vapour is responsible for the rapid shift of the mode of failure from cohesive to adhesive. The condensed water attacks the metal substrate on one hand causing the growth of iron oxide which leads to the weakening of the mechanical strength of the oxide layer, and the adhesive on the other. The corrosion products of the metal substrate introduces a considerable amount of ferric ions into the condensed water. These ions have a pronounced effect on the hydrolytic degradation of poly-ethylcyanoacrylate. The oxide layer grows in thickness and the hydrolytic degradation of the polymer spreads to the centre of the adhesive layer. As a result the bond strength falls continuously, resulting in the ultimate failure of the bond.

CONCLUSION

Steel-steel bonds rapidly lose strength when exposed to humid ageing because water vapour diffuses through the metal oxide/adhesive interface causing weakening of the oxide layer due to the growth of ferric oxide. This also may be accompanied by displacement of the adhesive from the bonding surface by water molecules. The adhesive strength may also be reduced by hydrolytic degradation of the adhesive, commencing at the interface and progressing towards the centre of the assembly. This process is catalysed by the corrosion products of the metal substrate in the condensed water at the interface. Bonds formed between polycarbonate substrates with cyanoacrylate adhesives are much less susceptible to humid environments because there is obviously no oxide layer present and thus the hydrolysis reaction does not proceed as rapidly as for the steel-steel bonds.

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