Adhesive properties of ethyl 2-cyanoacrylate containing small amounts of acetic acid as adhesion promoter

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The lap shear strengths of steel joints bonded with ethyl 2-cyanoacrylate adhesive containing various amounts of acetic acid have been determined, and an optimum adhesion promoting effect was found at an acetic acid content of 0.25% by weight. Further tests showed that adhesion promotion with acetic acid was dependent on the nature and surface treatment of various metal adherends, with selectivity being shown towards steel, stainless steel and duraluminium.

Key words: adhesive-bonded joints; adhesive strength; adhesion promoters; acetic acid; cyanoacrylate adhesives

Cyanoacrylates are one-component adhesives which cure by anionic polymerization in seconds at room temperature, forming strong adhesive bonds[1]. They find speciality application in industry as structural adhesives for metals, alloys, plastics, rubbers and ceramics, and unique application in medicine as surgical adhesives and coatings.

Possibly due to their almost universal adhesion and the high strength properties of the resultant adhesive bond, only a few studies have been reported in the literature regarding adhesion promotion in cyanoacrylates. Adhesion promoting action is attributed to the anhydrides of maleic and itaconic acids[2] and to the esters of gallic acid[3]. Schoenberg[4] described the adhesion promoting properties of the monocarboxylic acids. Of the compounds studied, the homologues of acetic acid proved to be most effective; amounts of 0.1 to 0.3% gave good results without detrimental effect on the curing time.

The objective of the present work was to determine the optimum quantity of acetic acid in ethyl 2-cyanoacrylate adhesive and the adhesive strength of various metal substrates bonded with ethyl 2-cyanoacrylate containing acetic acid, and to investigate the influence of surface treatment on the resultant adhesive-bonded joint.

Experimental details

The adhesives studied were based on ethyl 2-cyanoacrylate (ECA), synthesized according to Reference 5. The unmodified ECA was determined by gas chromatography to be 100% pure and contained 110 ppm hydroquinone and the specified amount of SO_2 as stabilizers. Glacial acetic acid was added directly to the ECA and mixed by shaking in polyethylene containers at room temperature.

The substrates for lap shear strength testing were lightly roughened with extrafine sandpaper and degreased with CH_2Cl_2. All of the results, unless otherwise specified, were obtained on bonded joints without further activation or treatment of the specimen surfaces.

The adhesives were applied as thin layers to one of the substrates, against which the other surface was aligned and manually pressed for one minute. Bonded specimens were cured for one day at room temperature (22–24°C) in air of humidity 55–65%. Testing of the bonded joints was carried out 24 hours after application of the adhesive.

Lap shear strength tests, performed on joints having dimensions specified in ASTM D-1002, were conducted at room temperature with a Zwick 1474 testing machine with a constant cross-head speed of 50 mm min^{-1}. Each of the reported values represents an average taken over 10 repeated experiments.

Fractography was performed with a Jeol T 200 scanning electron microscope (SEM) operating at 2.5 kV. For this purpose, failed specimens were cut into coupons approximately 5 × 5 mm with a cutting bar and fastened to the SEM stubs with conductive paste. To enhance conductivity approximately 20 nm of Au/Pd alloy was vacuum-evaporated onto the samples.

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Results and discussion

Fig. 1 shows the effect of acetic acid content on the lap shear strength of steel adherends (0.20% C) bonded with ECA monomer containing different amounts of SO_2 stabilizer. It can be seen that the optimum quantity of acetic acid was found to be 0.25% by weight in all three adhesives, which is well within the range of the previously reported data[4]. It is also clear from Fig. 2 that decreasing the SO_2 content in the monomer increases the effectiveness of acetic acid, that is SO_2 inhibits the adhesion promoting action of the acetic acid. However, SO_2 is vital for the bulk stability of the adhesive and has to be maintained in the range 40 to 80 ppm in order to produce effective stabilization without prolongation of the curing time of the adhesive[6].

Figs 3 and 4 show SEM photomicrographs of failed specimens bonded with pure ECA and ECA containing 0.25% acetic acid, respectively. In both cases the failure mode is interfacial. However, visual inspection of the surface, confirmed by SEM (Figs 3(a) and 4(a)), shows that the adhesive layer based on pure ECA is delaminated in such a way that large patches (up to 100 mm^2) are formed, while evenly spaced patches of considerably smaller dimensions are formed on both surfaces of the promoted adhesive layer. Since more energy is absorbed for cohesive destruction of the adhesive layer into small areas evenly distributed on both surfaces, this observation can in part explain the higher lap shear strength of the adhesive containing acetic acid. Furthermore, micrographs at higher magnification (Figs 3(b) and 3(c), 4(b) and 4(c)) reveal

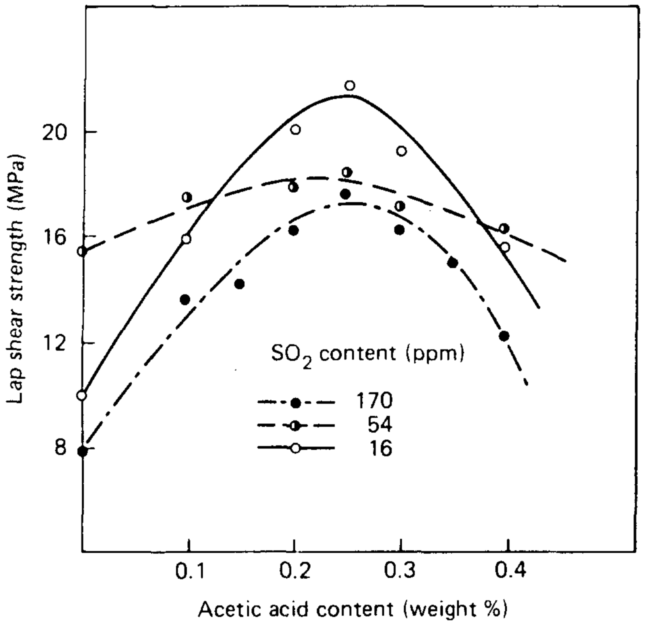


Fig. 1 Lap shear strength of steel joints bonded with ECA containing acetic acid as adhesion promotor

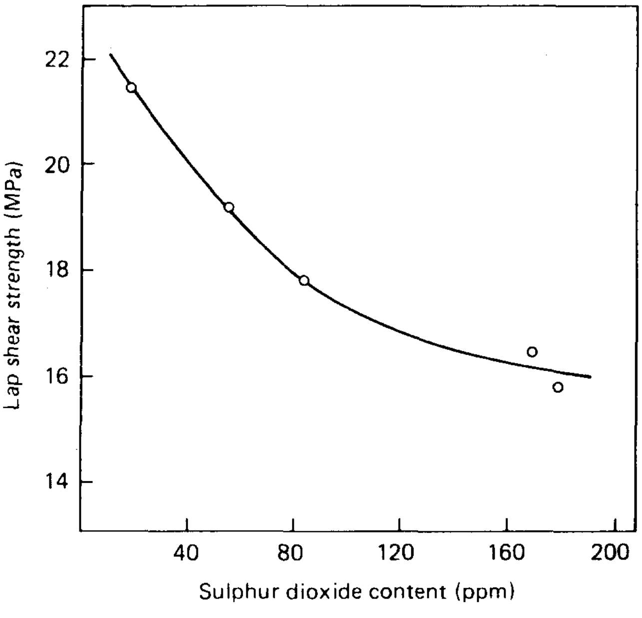
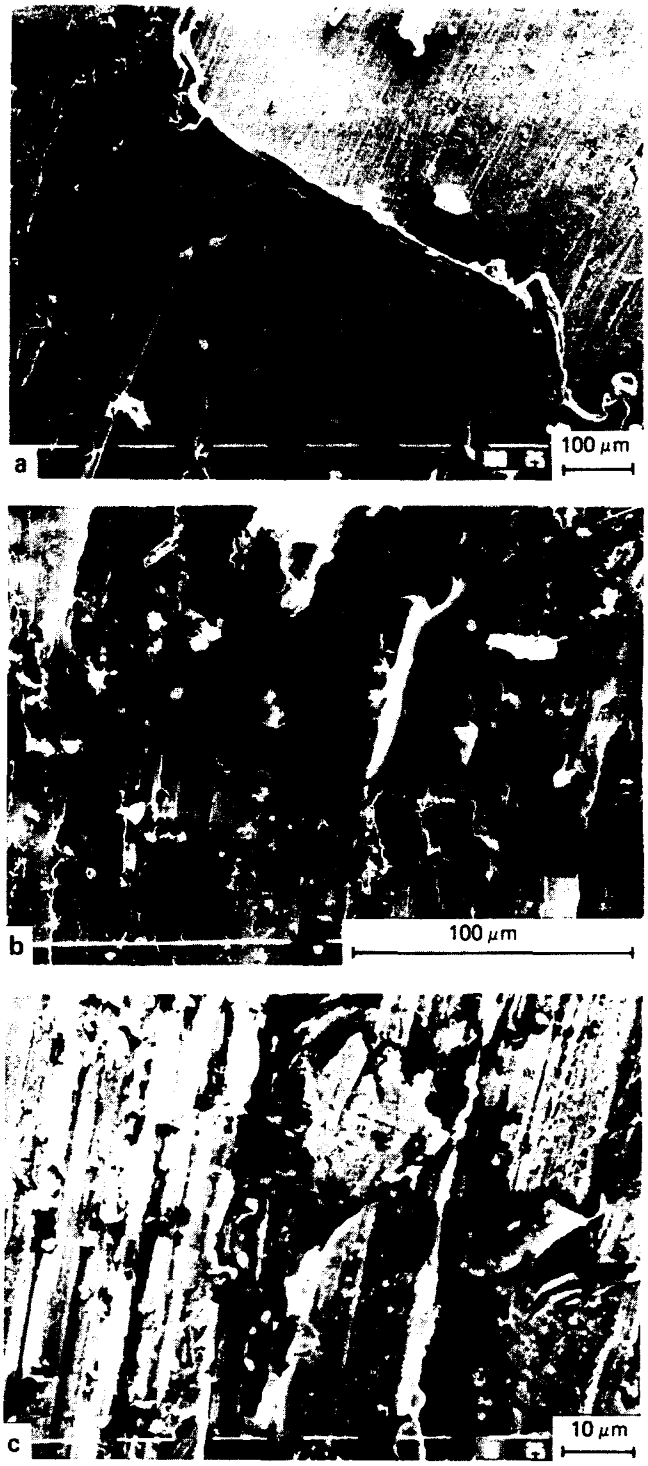


Fig. 2 Effect of SO_2 content on lap shear strength of steel joints bonded with ECA containing 0.25% acetic acid



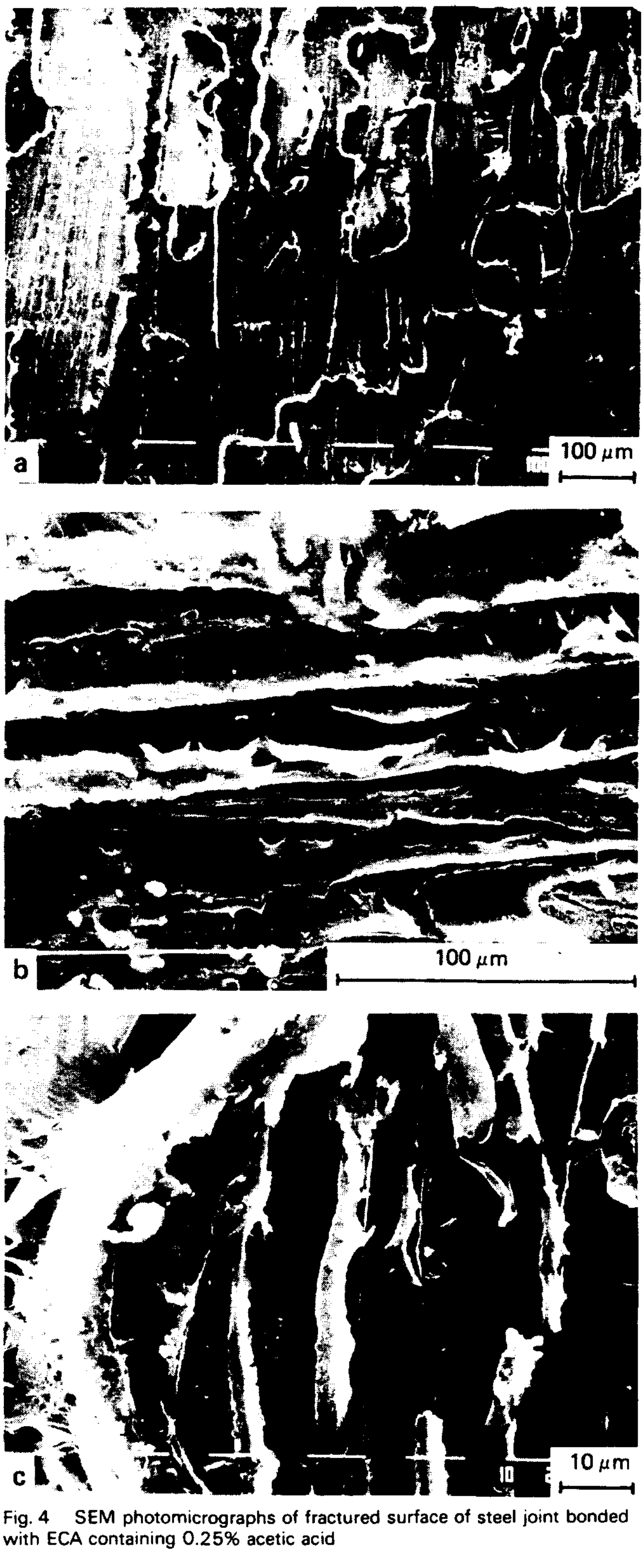


Fig. 4 SEM photomicrographs of fractured surface of steel joint bonded with ECA containing 0.25% acetic acid

a higher degree of plastic deformation in the cyanoacrylate bond containing adhesion promoter. The ridges of plastic deformation run parallel to the finish marks on the steel surface and are perpendicular to the applied stress. The observed difference of plastic deformation, which in turn absorbs a significant amount of strain energy, could also partially explain the difference in breaking strength.

Experiments were carried out to investigate the effects of surface treatment on the bonding of different metal substrates. Chemical treatment was in accordance with DIN 53 281, as outlined briefly in Table 1. Chemically treated and untreated substrates were bonded with pure ECA and ECA containing 0.25% acetic acid as adhesion promoter. In addition, adherend surfaces were activated with acetic acid in a procedure in which two drops of 0.25% by weight acetic acid solution in trichloroethylene were applied and spread on the substrate surfaces; after evaporation of the solvent, the joint was bonded with pure ECA. The results presented in Table 2 indicate that acetic acid promotes the adhesion of ECA to steel, stainless steel and duraluminium, but has a deterimental effect for copper and brass. Furthermore, the surface preparation of the specimens is of importance. For example, the best results for steel and stainless steel are obtained when the surface is only degreased, but not chemically treated. Etching, on the other hand, increases the lap shear strength of bonded duraluminium samples by 60%. The considerable discrepancy in strength properties observed when surface activation with acetic acid is employed is most likely due to the difficulty in controlling the amount of acetic acid left on the adherends prior to adhesive application.

Table 1. Surface treatments for various adherends

Substrate	Treatment
Steel (0.2% C)	Immersion in 17% H_2SO_4 at 80°C for 10 min, followed by neutralization in Na_2CO_3 and CH_3OH
Stainless steel	Immersion in 30% HCl for 15 min
Brass, copper and duraluminium	Immersion in aqueous solution of 27.5% H_2SO_4 and 7% $Na_2Cr_2O_7$ at 20°C for 5 min

It is well known that a metal surface is in fact a metal oxide surface. At ambient conditions the outermost surface oxygens hydrate to form a high density of hydroxyl groups. The hydroxyl-rich surface adsorbs and strongly retains several layers of bound water, as many as 20 molecular layers for aluminium, iron and copper[7]. In the case of the cyanoacrylates studied, this adsorbed water initiates a polymerization reaction leading to cure of the adhesive. If any chemical interaction takes place it would be between the hydrated oxide and the formed poly(cyanoacrylate) adhesive. Every oxide is characterized by the so-called isoelectric point of the surface. Carboxylic acid groups are used to promote adhesion to aluminium, steel and chromium, which have isoelectric points in the range 6 to 10, but are not effective for copper or its alloys. The mechanism of this action is the competition with and displacement of water molecules on the surface and the formation of strong hydrogen bonds with the oxide[7]. This leads to the assumption that acetic acid molecules help to displace the adsorbed water layers thus creating the possibility for direct contact of the polar groups of the adhesive with the oxide or through the acetic acid intermediate, which improves adhesion.

Recent work by Suetaka[8] can help explain the dependence of adhesion promotion with acetic acid on surface treatment. Infrared studies of thin cyanoacrylate films on aluminium surfaces have shown hydrogen bond formation between the cyanoacrylate polymer and the porous oxide layer, more precisely

Table 2. The effect of adhesion promotion, substrate nature and surface treatment on lap shear strength of joints bonded with ECA*

Substrate	Chemical treatment	Lap shear strength (MPa)		
		ECA	ECA containing 0.25% acetic acid	ECA, surface activated with acetic acid
Steel	No	9.7	19.1	11.7
	Yes	17.1	6.8	9.0
Stainless steel	No	11.3	18.0	12.5
	Yes	23.1	6.3	10.8
Copper	No	15.1	10.0	10.7
	Yes	6.4	5.8	2.2
Brass	No	12.2	6.7	9.3
	Yes	2.3	2.6	1.8
Duraluminium	No	7.8	8.4	6.5
	Yes	6.4	13.6	6.6

*ECA contains 110 ppm hydroquinone and 60 ppm SO_2

between the hydroxyl groups attached to the oxide and the carbonyl oxygen atom in the cyanoacrylate molecule. Furthermore it has been found that the structure of the oxide (changed through various chemical treatments of the metal surface) determines the orientation of the hydroxyl groups and therefore the orientation of the carbonyl group. The actual adhesive bond strength correlated with the carbonyl group orientation[8]. Based on these observations it can be assumed that a small amount of acetic acid contained in the cyanoacrylate adhesive plays a role in the hydrogen bond formation between the oxide and the adhesive, possibly changing the geometry and strength of the interaction. This can positively or detrimentally affect the molecular orientation in the polymer adhesive layer, influencing its mechanical strength.

Conclusions

Acetic acid acts as an adhesion promoter for ethyl 2-cyanoacrylate adhesives. Selectivity towards steel, stainless steel and duraluminium was found. Adhesion promotion with acetic acid is dependent on the surface treatment of the metal adherends.

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