

Assessment of the Adhesive Bond Properties of Allyl 2-Cyanoacrylate

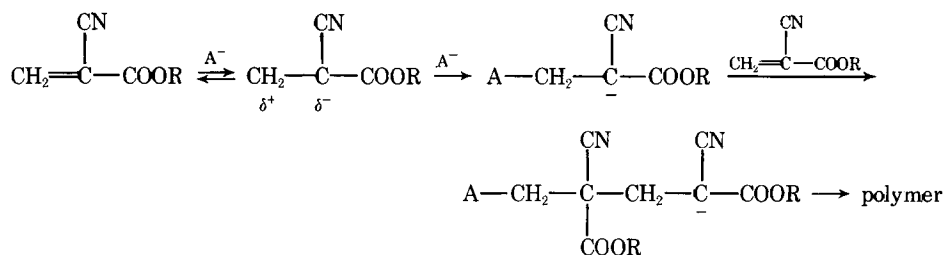
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Synopsis

The adhesive bond of allyl 2-cyanoacrylate between steel substrates has been analyzed and compared to that of ethyl 2-cyanoacrylate. Mechanical strength as well as thermomechanical, calorimetric, thermogravimetric, and dynamic mechanical response was observed. It was demonstrated that the allyl 2-cyanoacrylate bonds exhibit improved temperature resistance owing to the formation of heat-induced crosslinks in the adhesive layer, resulting in much improved lap-shear strengths. Scanning electron microscopy of the fracture surfaces showed that plastic deformation occurred in the allyl 2-cyanoacrylate adhesive after thermal aging, while interfacial and brittle failure dominated all other cases.

INTRODUCTION

Alkyl 2-cyanoacrylates (2-CA) are enjoying increased popularity as instant and specialty adhesives in industrial and consumer markets.¹ The adhesive action is a result of exothermal anionic polymerization initiated by water molecules adsorbed on the substrate²:



One of the properties of the resultant adhesive bond (imposing a limitation on practical utility) is low heat resistance (80°C) due to both the low glass transition temperature of the polymer and the onset of thermal degradation.² In an attempt to cope with that problem some cyanoacrylates containing an unsaturated bond in the ester radical of the molecule (R) were synthesized recently.³ The motivating assumption was that after the typical anionic curing of the resin, the adhesive bond would be able to undergo subsequent heat-initiated crosslinking, thus yielding a three-dimensional structure with improved thermal properties. The unsaturated cyanoacrylates indeed proved to have superior heat resistance⁴; the best results were obtained for allyl 2-CA.⁵

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The subject of this paper is to further quantify the properties of the allyl 2-CA adhesive bond. A variety of test procedures were employed to establish that, indeed, substantial property improvements could be realized over the alkyl 2-CA.

EXPERIMENTAL

The adhesives used were 100% pure allyl 2-CA and ethyl 2-CA, synthesized according to Ref. 3 and analyzed by gas chromatography.

The lap shear strength specimens had dimensions specified in DIN 53281/68. Steel substrates were roughened with extrafine sandpaper, degreased with CH_2Cl_2 , but not chemically treated. The adhesive was applied on one of the surfaces, against which the other substrate was subsequently manually pressed for 60 sec. The bonded joints were tested 24 hr after application of the adhesive in the tensile mode, with a constant cross-head speed of 50 mm/min. The ambient conditions were 20–22°C and 55–65% RH. Thermal treatments were carried out in an air circulating oven, after which the specimens were annealed in a desiccator at room temperature and then tensile tested as described above. The values presented in Table I are each the average of 10 lap shear tests.

The calorimetric, thermomechanical, and thermogravimetric experiments were conducted on a Perkin-Elmer DSC-2, TMS-2, and TGS-2. The sample used was a 0.56-mm adhesive layer, after removal from the bonded joints. The heating rate was 10°C/min, and N_2 was used for purging.

Viscoelastic measurements of the cyanoacrylate adhesive bonds⁶ were carried out with the Rheovibron viscoelastometer DDV-II-C. The adhesive layer between two lap-bonded steel plates had the following dimensions: length 30.0 mm, width 5.0 mm, and thickness 0.2 mm. It was subjected to a small nondestructive sinusoidal shear strain at 110 Hz and gradually heated from room temperature to 250°C at 1°C/min in N_2 atmosphere.

Fractography was performed with an Advanced Metals Research (AMR) Corporation model 900 scanning electron microscope (SEM) operating at 20 kV. For this purpose, the failed specimens were cut to approximately 1 × 1 cm with a cutting bar and fastened to the SEM stubs with a conductive copper tape. To enhance conductivity, approximately 20 nm of Au/Pd alloy was vacuum evaporated onto the samples. To enhance topographical features, the samples were inclined 20° from the incident electron beam. Rapid elemental analysis was obtained by an energy-dispersive x-ray fluorescence attachment (EDAX International model 707A) to the SEM.

TABLE I
Lap Shear Strength of Steel-Steel Bonded Joints

| 2-CA monomer | Lap shear strength, MN/m ² | | |
|--------------|---------------------------------------|----------------------|----------------------|
| | Initial | After 24 hr at 100°C | After 24 hr at 150°C |
| Allyl | 15.8 | 17.2 | 7.8 |
| Ethyl | 12.2 | 7.6 | 0 |

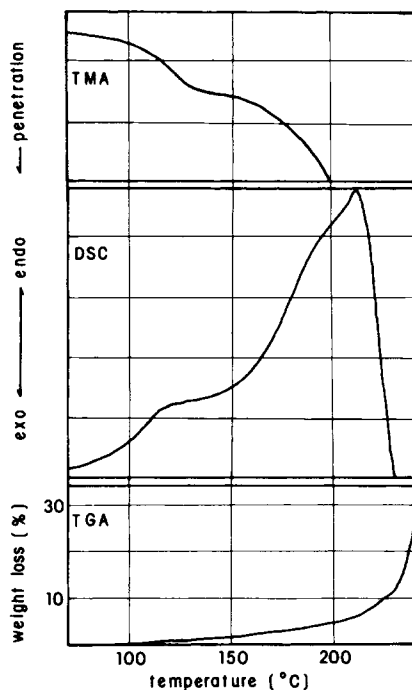


Fig. 1. TMA, DSC, and TGA of allyl 2-CA adhesive layer.

RESULTS AND DISCUSSION

The results presented in Table I compare the lap shear strength of steel-steel bonded joints made with either allyl or ethyl 2-CA adhesives. Thermal aging of the ethyl 2-CA bonds was found to decrease the strength at 100°C and to lead to complete loss of adhesive properties at 150°C. The allyl 2-CA adhesive bond, however, actually exhibits a slight increase in strength at 100°C and has significant residual properties at 150°C, well in the "safe" range for many technical applications.

The thermomechanical, calorimetric, and thermogravimetric response of the allyl 2-CA adhesive bond before thermal treatment is displayed in Figure 1 and was typical of that of the alkyl homologs (except for the DSC curve above 215°C, which shows an exothermic peak in the depolymerization range suggestive of allyl bond reaction). Thermal aging of the bond, however, causes a change in all three curves as discussed below.

Figure 2 demonstrates the increase in T_g of allyl 2-CA following exposures to a 100°C temperature. The softening point also increases from 106°C to 117°C after 24 h at 100°C. The weight loss of the adhesive layer at 250°C is reduced from 44% to 24% and to 2% after aging the bond for 24 h at 100 and at 150°C, respectively. For comparison, no change in T_g and softening point is observed for the ethyl 2-CA bonds. Also, the weight loss at 250°C is more than 95% for ethyl 2-CA, regardless of the thermal history of the adhesive bond. The observed difference in the behavior of the adhesive bonds can reasonably only be attributed to the occurrence of crosslinks in the allyl 2-CA polymer.

Figure 3 illustrates the behavior of the glass transition temperature of the allyl

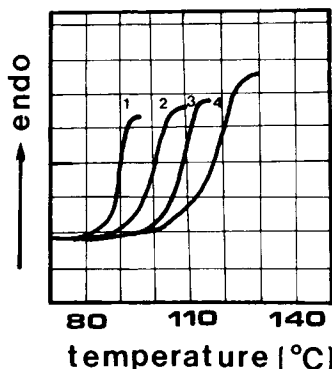


Fig. 2. Change of T_g of allyl 2-CA adhesive layer with time of aging at 100°C: (1) 0 min; (2) 30 min; (3) 150 min; (4) 24 hr.

2-CA adhesive bond as a function of isothermal time of aging. By obtaining the DSC isotherm of crosslinking at various temperatures (e.g., Fig. 4), a calculation of the percent cure was made at various times. Then it was possible to construct the kinetic curve for the crosslinking-induced cure as a function of T_g (Fig. 5).

Interesting results were observed on completing a series of nondestructive dynamic shear mechanical tests⁶ on our cyanoacrylate adhesive bonds. The dependence of the reduced shear storage modulus (relative to initial value) and $\tan \delta$ for ethyl 2-CA bonds (Fig. 6) on temperature clearly showed a glass transition point, a short rubbery plateau, and finally a rubbery-liquid flow. The glass transition-related decrease of the modulus and the short rubbery plateau (Fig. 7, curve 1) for the allyl 2-CA polymer adhesive bond is followed, on the other hand, by a modulus increase proportional to absolute temperature and characteristic of a rubbery network. Obviously, the increased mobility of the polymer chains above the T_g along with the thermal energy available had produced crosslinking reactions, changing the structure of the adhesive layer and its dynamic mechanical response.

The dynamic mechanical parameters of allyl 2-CA bond aged for 24 hr at 100°C

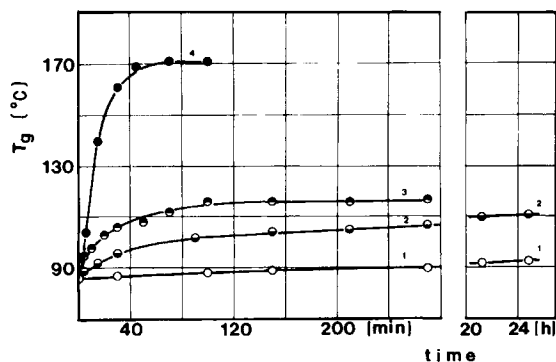


Fig. 3. Change of T_g of allyl 2-CA adhesive layer with time of thermal aging: (1) 60°C; (2) 100°C; (3) 150°C; (4) 200°C.

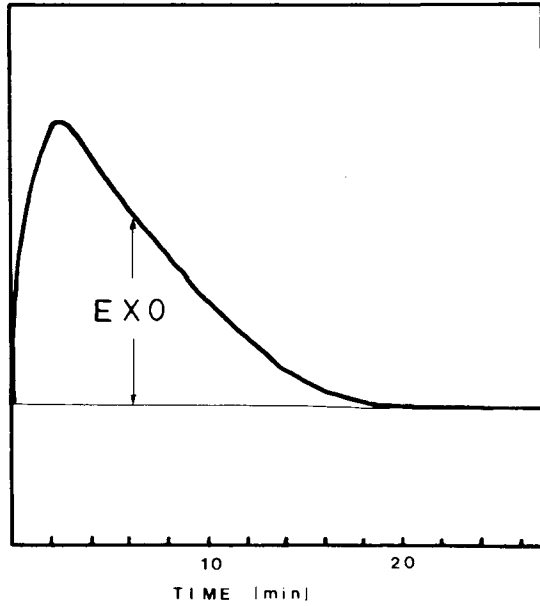


Fig. 4. Isotherm of crosslinking of allyl 2-CA adhesive layer at 200°C.

prior to testing (Fig. 7, curve 2) also indicate crosslinking was induced by the conditions of the experiment. However, this aging of the bond prior to testing had produced a shift of the damping peak to a higher temperature and a reduced intensity. Both of these changes are typical results of crosslinking. Aging for 24 hr at 150°C (Fig. 7, curve 3) produced polymers having dynamic response characteristic of a highly crosslinked three-dimensional structure.

A change in the adhesive joint structure was observed using SEM photomicrography of fractured steel-steel joints having different amounts of thermal aging. The adhesive (darker) and metal (brighter) surfaces were clearly distinguished with the help of EDAX. Intense iron peaks at 6400 and 7000 eV identified the bare steel surface, but when the electron beam was pointed at the adhesive surface, practically no iron response was obtained.

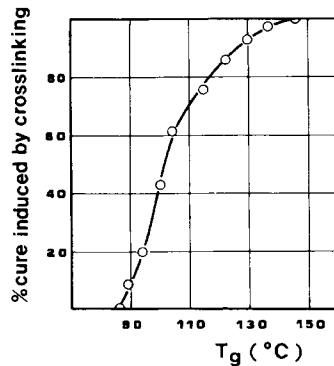


Fig. 5. Dependence of cure induced by crosslinking on T_g of allyl 2-CA adhesive layer.

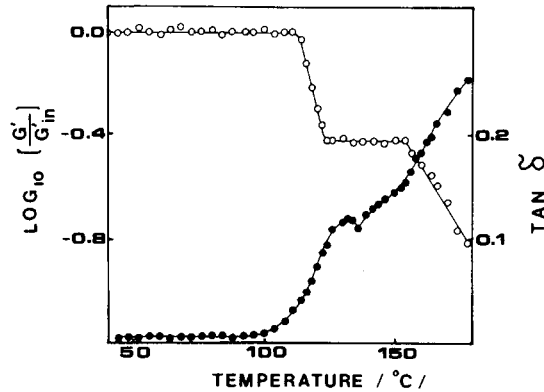


Fig. 6. Dynamic mechanical response of ethyl 2-CA adhesive bond.

Figure 8 contains SEMs of the ethyl 2-CA adhesive following different thermal treatments. The principal failure mode in all cases examined is interfacial with little plastic deformation. At 150°C, delamination due to melting of the adhesive occurred at negligible stress. Fractured specimens of the unheated allyl 2-CA adhesive bond have SEMs that looked very similar to those of ethyl 2-CA [Fig. 9(a)]. Similar failure modes are suggested. The ~30% greater strength of the allyl 2-CA must be due to its relatively higher bulk elastic properties. Aging allyl

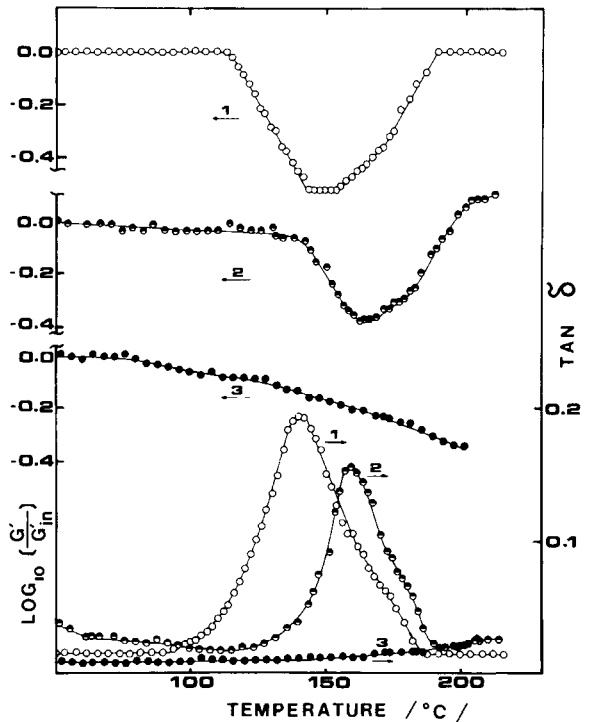


Fig. 7. Dynamic mechanical response of allyl 2-CA adhesive bond after thermal aging: (1) 20°C; (2) 100°C; (3) 150°C.

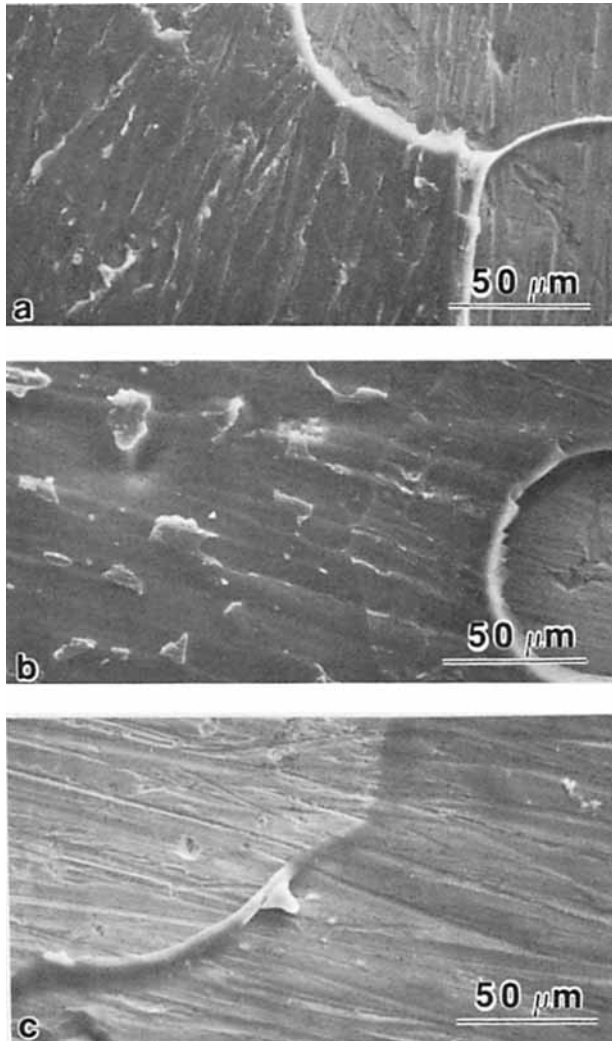


Fig. 8. SEM photomicrographs of the fracture surface of ethyl 2-CA adhesive joints: (a) room temperature; (b) after 24 hr of aging at 100°C; (c) after 24 hr aging at 150°C.

2-CA bonds at 100°C [Fig. 9(b)] and 150°C [Fig. 9(c)], however, brings about a dramatic change in irreversible micromechanisms in the failure process as evidenced in the SEMs. Ridges of plastic deformation may be noted in these figures. They run parallel to the finish marks spaced about 1 μm apart on the steel substrates (perpendicular to the applied stress). The crosslinking process has produced a much more resilient like failure mode.⁴

The stress concentrations at the tops of the finish scratches probably initiated plastic mechanisms that absorbed significant amounts of strain energy, leading to increased breaking strength. Packham has recently elaborated this point in the case of polyolefin bonds to high-surface-area chemically etched copper and steel substrates.^{7,8}

In conclusion, it has been demonstrated by lap shear strength testing, DSC,

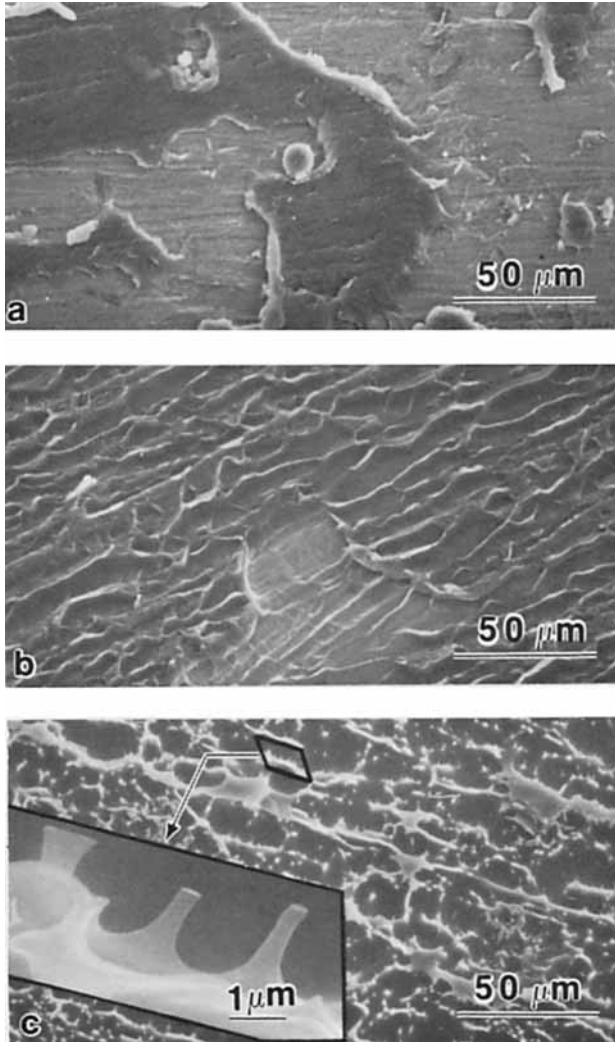


Fig. 9. SEM photomicrographs of the fracture surface of allyl 2-CA adhesive joints: (a) room temperature; (b) 24 hr aging at 100°C; (c) 24 hr aging at 150°C.

TMA, TGA, dynamic mechanical testing, and SEM that the allyl 2-CA adhesive bond exhibits improved thermal resistance when compared to ethyl 2-CA. These improvements are a result of heat-induced crosslinking reactions.

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