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# Adhesive Bond Properties of Ethyl-2-cyanoacrylate Modified with Poly(methylmethacrylate)

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The mechanical properties of the adhesively bonded joints with ethyl-2-cyanoacrylate and ethyl-2-cyanoacrylate modified with poly(methylmethacrylate) were determined. The modifier lowers tensile stiffness, increases deformability and relaxation of the adhesive bond and improves impact resistance. A morphological structure similar to an interpenetrating network system is suggested which arises from the rapid polymerization of the solvent. The results obtained may be helpful for the design of joints with cyanoacrylate bonding.

**KEY WORDS** Adhesively bonded joints; cyanoacrylate; ethyl-2-cyanoacrylate; PMMA; mechanical properties; glass transition; interpenetrating network.

## INTRODUCTION

The ability of cyanoacrylates to bond most materials in seconds has produced spectacular growth in their production and application.<sup>1</sup> One of the ways to overcome the poor impact resistance of their adhesive-bonded joints has been the introduction of polymer modifiers into the cyanoacrylate monomer. Poly(methylmethacrylate),<sup>2</sup> poly(butadiene-co-acrylonitrile)<sup>3</sup> and copolymers of methyl acrylate and ethylene<sup>4</sup> are some of the polymer modifiers which were found to decrease the brittleness of the resultant bond.

The aim of this paper is to study the influence of poly(methylmethacrylate) modifier of ethyl 2-cyanoacrylate on the stiffness, strength, deformation characteristics and relaxation properties of the resultant adhesive bond between steel specimens.

## EXPERIMENTAL

100% GC pure ethyl 2-cyanoacrylate (ECA) was obtained by distillation of the commercial product Kanokonlit E. It was stabilized with 250 ppm hydroquinone and 200 ppm p-toluenesulfonic acid. Modified adhesives were obtained by dissolving specified amounts of poly(methylmethacrylate) into the ethyl 2-cyanoacrylate monomer by mixing at 50°C. The poly(methyl methacrylate) (PMMA) was commercial grade bulk polymer with molecular mass of  $1.5 \times 10^6$ .

All mechanical tests were performed on steel (0.2%C content) bonded joints. The surfaces to be bonded were roughened with Igel 400 sandpaper and degreased with trichloroethylene. Chemical treatment or activation were not employed. Universal testing machine Zwick 1474 was used. Tensile shear strength was determined in accordance with ASTM D-1002 on single overlap specimens. After adhesive application the joint was clamped and left for 24 h at 20–22°C and 55–65% relative humidity. The crosshead speed of testing was 50 mm/min. The reported values are the averages of 15 tests. Tensile strength was determined in accordance with ASTM D2095 on cylindrical specimens. No clamping was employed. All other conditions were as specified above. Impact strength was determined in accordance with ASTM 950–72. The test specimen for shear strain determination had dimensions shown on Figure 1.<sup>5,6</sup> The thickness of the glue-line (0.05 mm) was controlled with the use of calibrated copper wire. The test specimen for tensile strain determination is shown on Figure 2.<sup>7</sup> This multilayer structure was chosen because it provides a means for increasing the absolute value of deformation within measurable limits. All adhesive layers had a thickness of 0.05 mm controlled with calibrated copper wire.

To obtain the necessary co-axiality a specially cut Teflon jacket was used for assembly of the specimens after adhesive application.

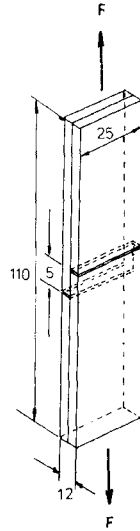


FIGURE 1 Test specimens for shear strain determination (Ref. 5,6) (Dimensions in mm)

For determination of the real proportionality limit in the stress-strain dependence a cycle of "loading-pause-unloading-pause" was employed. The rate of loading and unloading was 0.025 mm/min. The loaded pause (600 sec) was used as the criterion for appearance of visco-elastic strain. The unloaded pause (600 sec), on the other hand, was a measure of the reversibility of the strain. Strain was measured with an Instron G-51-11-M extensometer and the strain/time dependence was recorded with the help of additional Tacussel EPL-2 recorder. Relaxation experiments were conducted on bonded specimens with dimensions according to ASTM D1002. The bonded specimens were loaded in tension with 100 mm/min

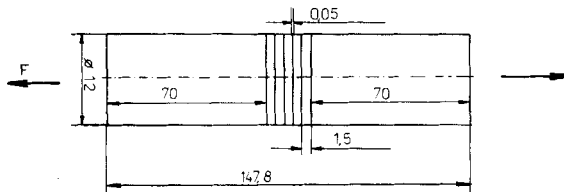


FIGURE 2 Test specimens for tensile strain determination (Ref. 7) (Dimensions in mm)

crosshead speed at  $22 \pm 1^\circ\text{C}$  to a constant strain and kept there for 60 sec. The time required for achievement of stress equilibrium was recorded. The relaxation time was calculated by the following formula:

$$\sigma = \sigma_0 e^{-t/\tau} \quad (1)$$

where  $\tau$ —relaxation time

$\sigma_0$ —initial stress at time  $t = 0$

$\sigma$ —stress after time interval  $t$

The calorimetric experiments were conducted on a Perkin-Elmer DSC-2C. The samples used were from the adhesive layer, removed after failure of bonded joints. The scanning rate was 20 deg/min.

## RESULTS AND DISCUSSION

Figure 3 shows the stress-strain curves for bonded joints in the shear tensile loading mode. In the case of the bond based on pure ECA

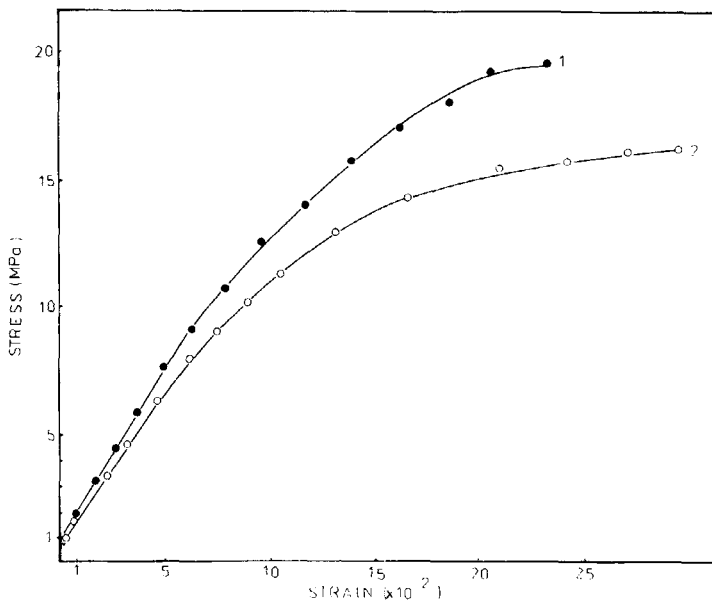


FIGURE 3 Stress-strain relationship in shear mode for cyanoacrylate adhesive bonds 1—pure ECA 2—ECA containing 4 wt.% PMMA

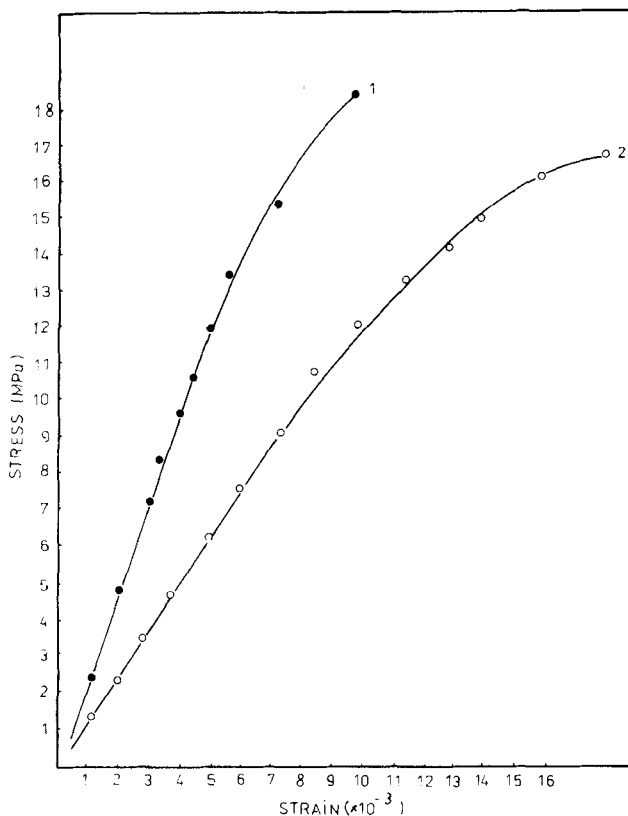


FIGURE 4 Stress-strain relationship in tensile mode for cyanoacrylate adhesive bonds 1—pure ECA 2—ECA containing 4 wt% PMMA

(curve 1) the relationship is linear until 40% of failure stress is reached. The visco-elastic strain component is evident in the stress interval of 40 to 70% of failure. Creep is registered when stress values are over 70% of failure stress. The bond based on modified ECA (curve 2) shows proportionality up to 48% stress value, visco-elastic strain in the 48–73% interval and creep when the stress surpasses 73% of failure value. At failure the strain for the pure ECA bond is 24%, while that of modified ECA reaches 30%.

The stress-strain curves for normal tension are shown on Figure

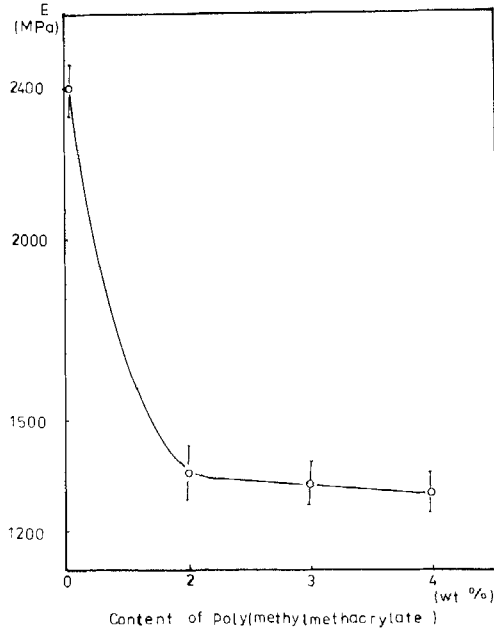


FIGURE 5 Tensile stiffness of bonded joints as function of PMMA content in ECA

4. The linear relationship is maintained until 63% of failure stress is reached for pure ECA bond (curve 1) and 56% of failure stress for the modified ECA bond (curve 2). The visco-elastic strain component is registered in the stress interval 63–80% of failure for the ECA bond and 56–70% of failure for the modified ECA bond. Creep is registered at stress above 80% and 70% of failure stress, respectively. At failure, the strain for the pure ECA bond is 1.0% and 1.8% for the modified ECA bond. When the data for shear and tension are compared it is evident that the strain of the adhesive bond in the shear mode is one magnitude higher than that in the tensile mode. The incorporation of PMMA into the ECA adhesive increases the susceptibility of the bond to deformation.

Figure 5 shows the data for the stiffness of modified and unmodified ECA bonds. The stiffness values were determined from the mid-range of the linear proportionality part of the stress-strain relationship. Tensile stiffness falls by almost half upon modification

TABLE I  
 Physico-mechanical properties of ethyl 2-cyanoacrylate adhesive bonded joints

Adhesive	Tensile shear strength (MPa)	Strain at failure (shear) (%)	Tensile strength (MPa)	Strain at failure (tension) (%)	Impact strength (kJ/m <sup>2</sup> )	Tensile stiffness (MPa)
ECA	19	24	30	1.0	4.3	2400
ECA contg. 4 wt. %PMMA	19	30	30	1.8	6.2	1303

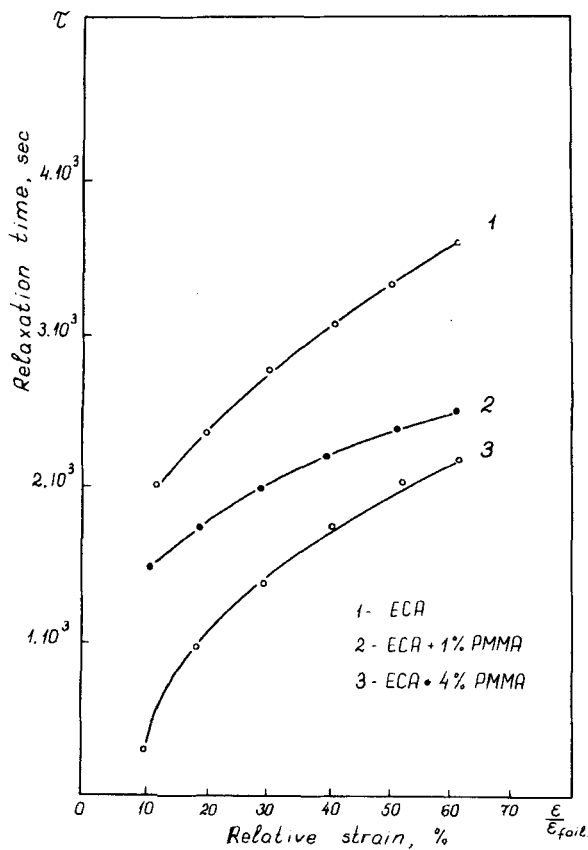


FIGURE 6 Stress relaxation at constant strain of ECA adhesive bonds



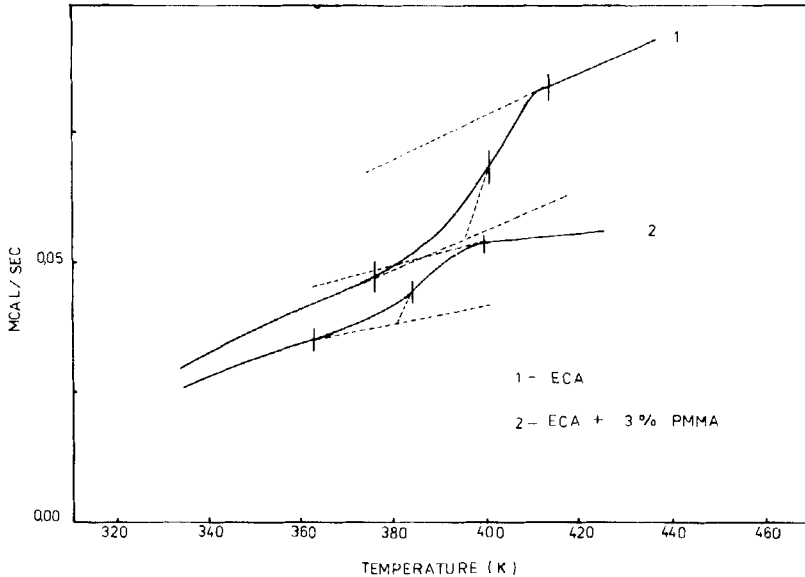


FIGURE 7 Glass-transition of ECA adhesive bonds

of the adhesive with PMMA, then levels off and is not further considerably lowered with the increase of polymer modifier quantity above 2 wt. %.

The influence of PMMA modifier is demonstrated also by the mechanical properties of the adhesive joint, summarized in Table 1.

The introduction of a small amount of PMMA does not reduce the tensile or shear strength but increases the impact strength of the bond and its deformability.

The data for stress relaxation at constant strain (Fig. 6) show a lower relaxation time for the bond based on modified cyanoacrylate. These results correlate well with the DSC study of adhesive removed from the bond layer (Fig. 7). The glass-transition of the ECA adhesive bond is 127°C. The bond containing 3 wt. % PMMA shows a  $T_g$  of 111°C. The specific heat of the glass-transition of the modified adhesive is half of that for the ECA. This shows that the incorporation of high molecular mass PMMA into ECA produces a mild plasticization of the adhesive bond.

The higher deformation susceptibility, the lower stiffness, increased relaxation ability and single glass-transition point of the

adhesive based on ECA modified with PMMA lead to the assumption that a morphological structure, similar to that of an interpenetrating network system may be formed, as a result of the rapid polymerization of the PMM's solvent.

The data obtained in this study provide the necessary information for practical stress determination in designing cyanocrylate bonded joints bearing static loads.

## References

1. *Japan Adh. Ind. Book* (Tokyo, 1985), p. 57.
2. D. L. Kotzev and L. B. Dicheva, *1st Nat. Conf. Chemistry* (Sofia, 1985), p. 415.
3. V. Kabaivanov, D. Kotzev *et al.*, *Bulgarian Patent* 29, 489, (1979).
4. J. T. O'Connor, *US Patent* 4, 440, 910, (1984).
5. J. P. Jeandrau, *Int. J. Adh Adhesives* 6(4), 229–231 (1986).
6. W. Althof and W. Brockmann, *Adh. Age* 20(11), 27 (1977).
7. A. E. Freidin, *Strength and Durability of Adhesive Joints* (Himia, Moscow, 1981), pp. 113–114.