

Strength, deformation and relaxation of joints bonded with modified cyanoacrylate adhesives

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The introduction of high molecular weight poly(methyl methacrylate) or poly(butadiene-co-acrylonitrile) into ethyl 2-cyanoacrylate produced viscous adhesives with a homogeneous or heterogeneous structure after cure. Steel joints bonded with these adhesives are shown to have improved tensile shear strength, deformability and stress relaxation of bonds compared with pure cyanoacrylate adhesive. Poly(methyl methacrylate)-modified adhesive is recommended for static load-bearing joints while poly(butadiene-co-acrylonitrile)-modified adhesive is more suited to cyclic or vibrating loads.

Key words: adhesives; modified cyanoacrylates; adhesive-bonded joints; adhesive strength; mechanical tests

One method which has been used to improve the properties (such as viscosity and brittleness after cure) of cyanoacrylate adhesives has been the incorporation of polymeric material into the liquid cyanoacrylate monomer. As early as 1957, Coover *et al*¹ used poly(methyl methacrylate) (PMMA) as thickener for cyanoacrylate adhesives. Introducing high molecular weight PMMA into the cyanoacrylate achieves the desired viscosity of the adhesive composition, even at low modifier content, without detrimental effect on the setting time or strength properties². Studies on the properties of resultant bonds led the present authors to the supposition that the morphological structure of the cured adhesive resembled an interpenetrating network system³. Toughened cyanoacrylates are obtained when elastomeric polymers, such as methacrylate-butadiene-styrene terpolymers⁴, butadiene-acrylonitrile copolymer⁵, or methyl acrylate-ethylene copolymer⁶, are incorporated into the cyanoacrylate composition. As well as achieving the desired viscosity modification, the elastomers impart significant improvement on impact resistance, peel strength, strength at higher temperatures, and resistivity to multiple cyclic deformations of the adhesive bond^{6,7}. Although no specific data are reported it can be assumed that the elastomeric phase is finely dispersed in the cured cyanoacrylate matrix, resembling the structure of toughened acrylic adhesives which has been well described. In these, the rubber phase (particle

size $\approx 1 \mu\text{m}$) is finely dispersed in the cured acrylic matrix⁸. Thus, the applied load is borne by the glassy portion of the structure while the fracture energy is absorbed and dissipated in the rubbery phase which distorts during the dissipation of that energy⁹.

The objective of the work described below was to study and compare the strength, strain and relaxation properties of adhesive bonds based on ethyl 2-cyanoacrylate (ECA) adhesive modified with PMMA or poly(butadiene-co-acrylonitrile) (PBAN).

Experimental details

100% GC pure ECA, obtained by distilling the commercial grade product (Kanokonlit E, Bulgaria) was stabilized with 250 ppm hydroquinone and 200 ppm p-toluenesulphonic acid. The PMMA-modified adhesives were obtained by dissolving specified amounts of commercial grade PMMA (bulk polymer, molecular weight 1.5×10^6) directly into the ECA by mixing at 50°C. The PBAN (commercial brand, Perbunan 3807NS from BASF, FRG) was first dissolved in distilled and dried CH_2Cl_2 to form a 10 weight % solution and then mixed with the ECA. The CH_2Cl_2 was removed under vacuum (5 mmHg) at 40°C leaving the PBAN-modified adhesive composition.

The amount of modifier used and the viscosities of the compositions obtained are given in Table 1.

Adhesive-bonded steel (0.2% C content) joints were

Table 1. Viscosity of adhesive compositions

Modifier		Viscosity at 20°C (cP)
Type	Amount (weight %)	
PMMA	—	2.5
	1	23
	2	52
	3	150
	4	495
PBAN	1	25
	3	96
	5	180
	8	450
	10	620

PMMA poly(methyl methacrylate)
PBAN poly(butadiene co-acrylonitrile)

used in all the mechanical tests. The surfaces to be bonded were roughened with Igel 400 sandpaper and degreased with trichloroethylene (chemical treatment or activation were not employed). After application of the adhesive the joint was clamped and left for 24 h at

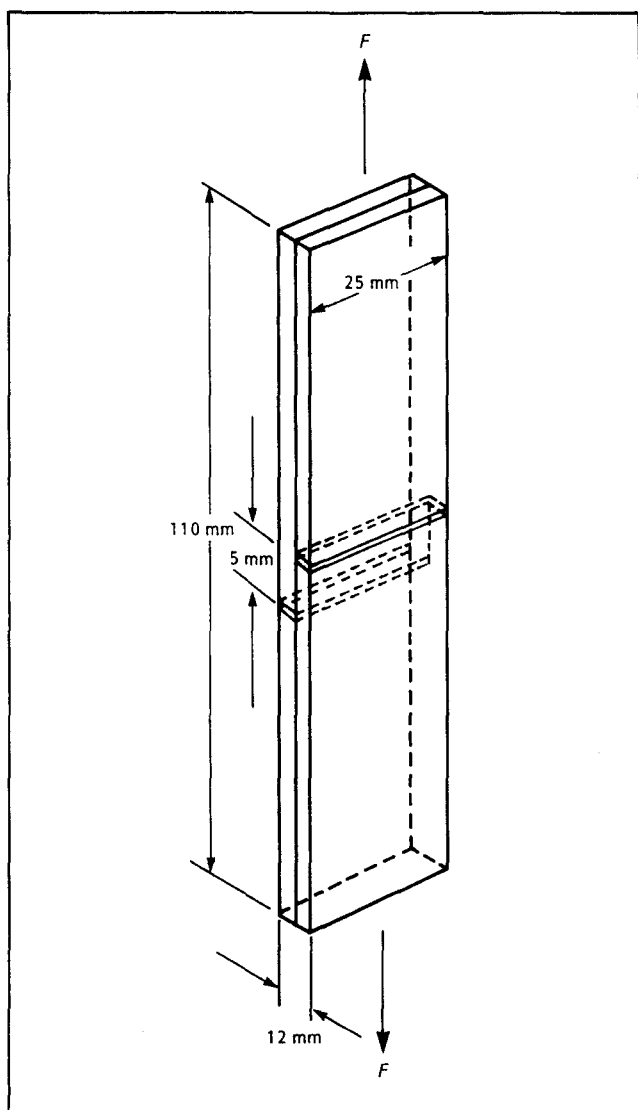


Fig. 1 Test specimen for shear strain determination (References 10, 11)

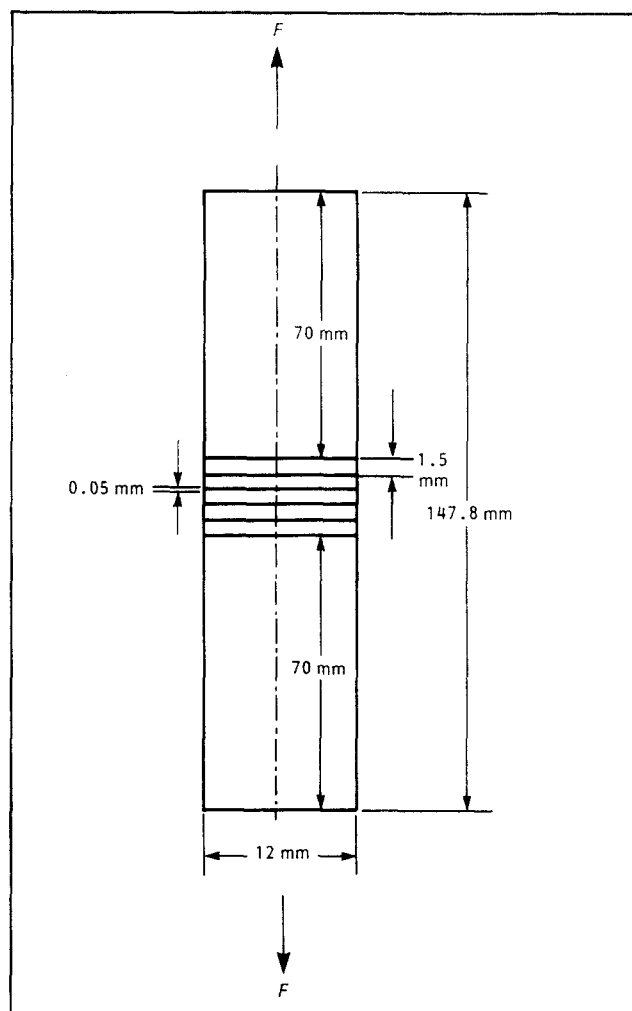


Fig. 2 Test specimen for tensile strain determination (Reference 12)

20–22°C and 55–65% RH. The thickness of the glue-line (0.05 mm) was controlled with the use of calibrated copper wire.

Tensile shear strength was determined in accordance with ASTM D-1002 on single overlap specimens. A Zwick 1474 Universal testing machine was used.

The test specimen for shear strain had dimensions as shown in Fig. 1^{10, 11}. The rate of loading was 0.025 mm min⁻¹.

The relaxation modulus was determined with the help of the test specimen for tensile strain determination (shown in Fig. 2)¹². The multilayer structure was chosen because it provided a means for increasing the absolute value of deformation within measurable limits, since cyanoacrylates polymerize only in very thin films. It consists of five cylindrical discs, 12 mm in diameter and 1.5 mm thick, assembled between two cylindrical rods of the same diameter. The adhesive is applied between the discs and rods, thus providing six adhesive lines. All adhesive layers had thicknesses of 0.05 mm. To obtain the necessary co-axiality, a specially-cut Teflon jacket was used for the assembly of the specimen after adhesive application. The specimen was loaded at a rate of 20 mm min⁻¹ to a specified deformation and held loaded for 600 s, after which, stress and deformation values were recorded.

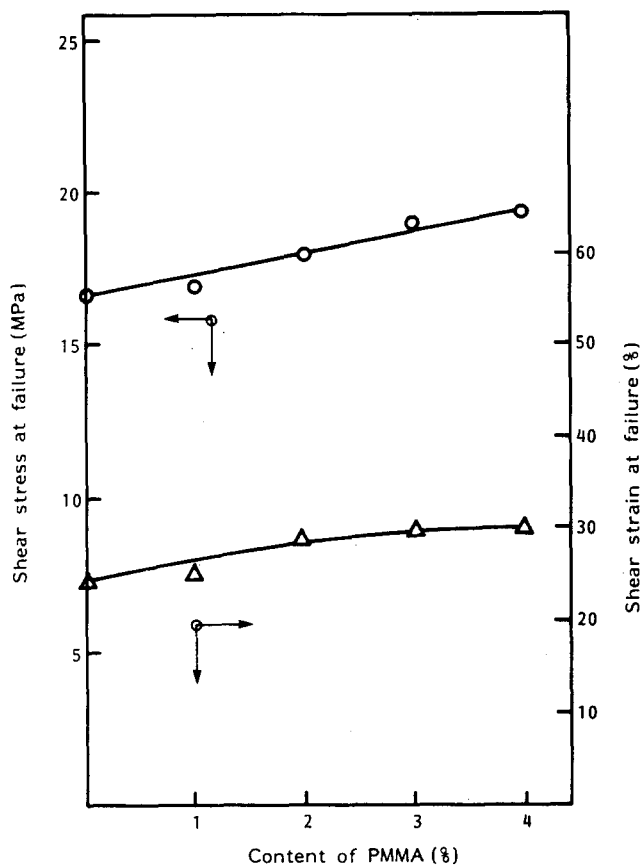


Fig. 3 Dependence of shear stress and shear strain on content of PMMA in adhesive

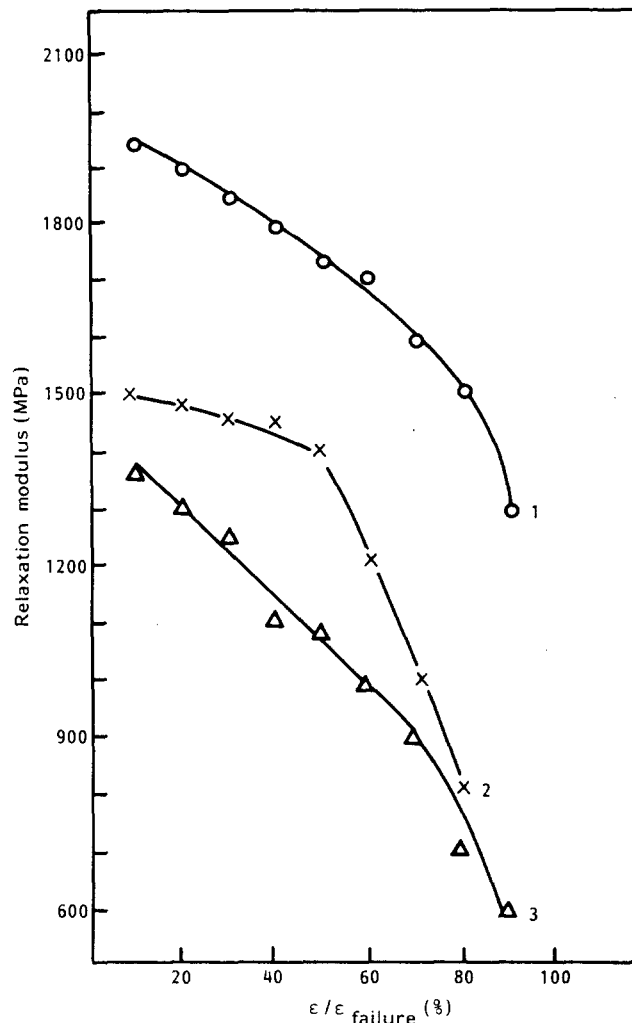


Fig. 5 Dependence of relaxation modulus on relative strain: 1, pure ECA; 2, ECA containing PBAN (3 weight %); 3, ECA containing PMMA (4 weight %)

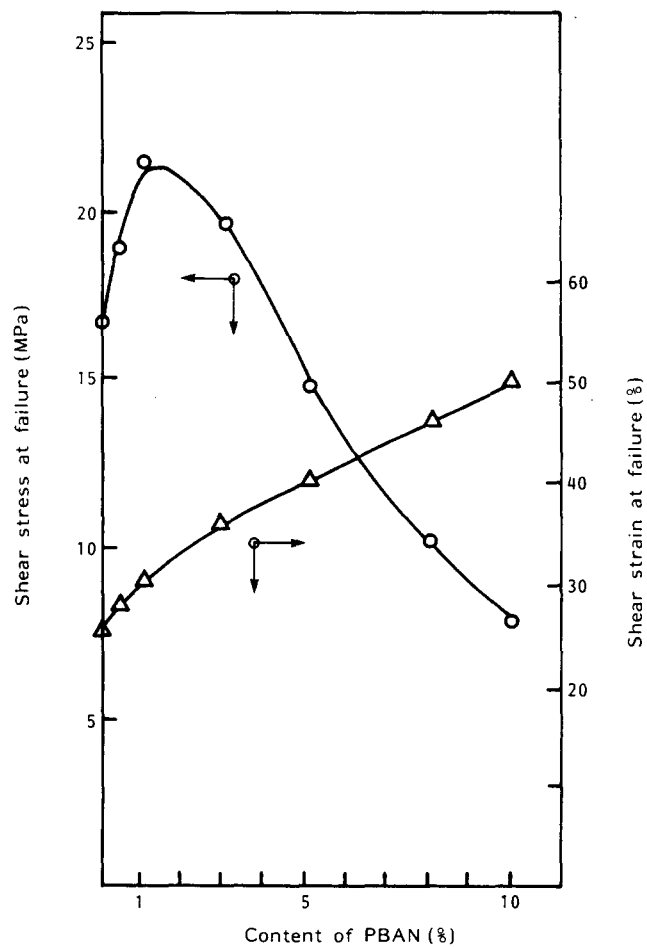


Fig. 4 Dependence of shear stress and shear strain on content of PBAN in adhesive

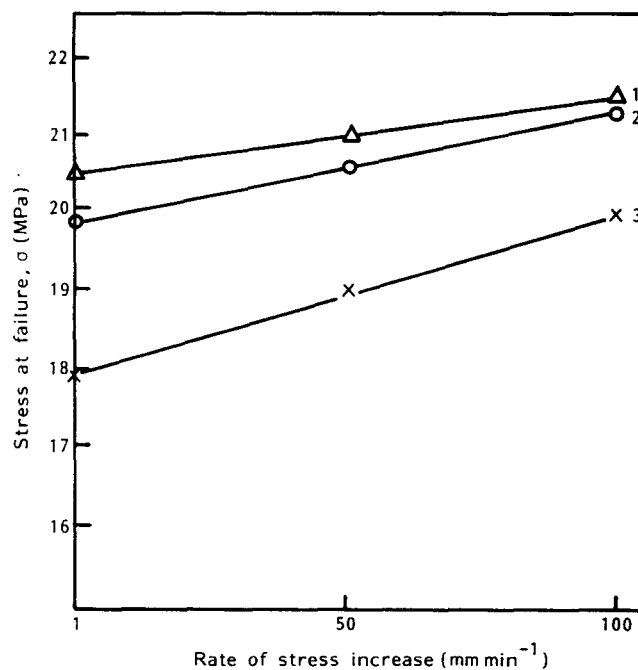


Fig. 6 Dependence of stress at failure on rate of applied load: 1, ECA containing PBAN (3 weight %); 2, ECA containing PMMA (3 weight %); 3, pure ECA

Strain was measured using an Instron G-51-11-M extensometer and the strain/time dependence was recorded with the help of an additional Tacussel EPL-2 recorder.

Results and discussion

The dependence of tensile shear strength and relative elongation at break of bonded joints on the content of PMMA in the ECA adhesive and PBAN in the ECA adhesive is shown in Figs 3 and 4 respectively. Increasing the content of PMMA causes slight and almost uniform increase of the tensile shear strength and deformability of the bond. PBAN-modified adhesive show increased strength when the elastomer content is in the range 0.5–4.0 weight %, with a well pronounced maximum at 1.0 weight %. Further increase in modifier content affects the strength value detrimentally. The deformability of the adhesive bond increases with the increase of PBAN content. On comparing Fig. 3 with Fig. 4 over the 0–4 weight % modifier content range, it can be seen that the adhesive containing PBAN has better strength and a more pronounced susceptibility of the joint to deformation.

The change of relaxation modulus with the increase of the deformation relative to deformation at failure of adhesive bond ($\varepsilon/\varepsilon_{\text{failure}}$) is shown in Fig. 5. The curves for pure ECA bonds and PMMA-modified ECA bonds have similar shape. The relaxation modulus steadily decreases in value up to 70–80% of failure strain; above this deformation its value drops sharply. In the case of PBAN-modified adhesive the decrease of modulus value up to $\varepsilon/\varepsilon_{\text{failure}} = 50\%$ is less pronounced, but falls steeply at higher values ratios. This is associated with the change of mechanism of the deformation process caused by the beginning deformation of the elastomeric phase.

Fig. 6 shows the dependence of the tensile shear strength of bonded joints on the rate of applied stress. Decreasing the stress rate decreases the value of the tensile shear strength for all adhesive systems. The PBAN-modified adhesive bonds, however, are the least affected.

Conclusions

The data obtained in this study confirm practical results reported previously^{2,5} for cyanoacrylate adhesives containing PMMA or PBAN. The modified adhesives display improved strength properties, deformation susceptibility, and stress relaxation. Adhesives modified with PMMA would be appropriate for static load-bearing joints whereas joints bonded with PBAN-modified cyanoacrylate adhesives could better withstand cyclic or vibrating loads.

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