

The Effect of Heat on the Molecular Weight of Poly(ethyl 2-Cyanoacrylate) Adhesive

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Synopsis

Steel-steel ethyl 2-cyanoacrylate adhesive bonds have been thermally aged and the polymeric material isolated from the glue line. Molecular weight measurement by gel permeation chromatography suggest that a significant degree of post-curing occurs followed by a slight decrease in molecular weight. This decrease in molar mass is not considered large enough to explain the observed decrease in bond strength. It is postulated that poly(ethyl 2-cyanoacrylate) undergoes thermal degradation in a manner similar to that reported for poly(methyl methacrylate). The loss in bond strength is thought to be due to the disruption of the polymer-metal interface by monomer molecules produced during the thermal depolymerization.

INTRODUCTION

Alkyl 2-cyanoacrylates are liquid monomers which polymerize extremely rapidly under the influence of a basic catalyst. These materials are so sensitive to the presence of bases that the reaction may be initiated by water or ethanol. This apparent tendency towards instant polymerization has led to the use of these materials as adhesives. Polymerization is brought about by small amounts of moisture on the surface of the adherends. Pepper¹⁻⁴ has carried out detailed studies of the kinetics and mechanism of the polymerization of these materials with various initiators. It was shown in all cases that the reaction was rapid and proceeded via an ionic mechanism. Covalent bases in some instances gave rise to living polymers. These are believed to involve propagation by a zwitterionic species.

Many patents⁵ have been published regarding the performance and stability of cyanoacrylate compositions, but information regarding the properties of the polymer formed in these adhesive applications is scarce.⁶⁻⁹ The main problem associated with cyanoacrylate adhesives is their poor heat stability.¹⁰ Loss in bond strength has been reported to occur at temperatures as low as 60°C.⁷ The present work describes an attempt to study the effect of thermal ageing on the molecular weight of poly(ethyl 2-cyanoacrylate) formed in steel-steel bonds.

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EXPERIMENTAL

Materials

Mild steel laps (ASTM D 1002-64, $100 \times 25 \times 1.5$ mm) and ethyl 2-cyanoacrylate were supplied by Loctite (Ireland) Ltd. The monomer was stabilized with methanesulfonic acid (20 ppm) and hydroquinone (100 ppm).

Bond Preparation

The steel laps were degreased by immersion in trichlorethylene for 10 min. This was repeated three times and the laps were wiped with a lint-free tissue. A bonding area was marked on each specimen by drawing a pencil line 12 mm from the end of the lap. The monomer was applied dropwise to the bonding surface until it was completely covered. The marked area of a second lap was placed over the corresponding "glued" portion and a lap joint with a 300 mm^2 area formed. The bond was pressed together firmly, held by two spring loaded clamps designed to produce a pressure of 5 psi and left to cure for 24 h.

In total, 100 bonds were prepared in this way. The bonds were placed in an oven at 90°C . Twenty bonds were removed after 4, 8, 12, 24, and 48 h, and their tensile shear strength was determined using an Instron Universal Testing Instrument Model 1102 at ambient temperature. Immediately following the breaking test, the cured polymer was collected by removing the adhesive from the steel laps using a sharp bladed scraping device. Any metal particles produced during this process were removed with the aid of a magnet. The adhesive scrapings from twenty bonds were dissolved in acidified acetone (20 mL, 1% w/v hydrochloric acid). The solution was filtered using a sintered glass crucible and the polymer precipitated by the addition of 1% (w/v) hydrochloric acid in methanol (70 mL). It was found that 20 lap joints were required to give 100 mg of polymer.

Molecular Weight Determination

Molecular weights were measured using a Perkin-Elmer Gel Permeation Chromatograph, Model Series 10, with a PL Gel mixed bed column. The polymer was dissolved in tetrahydrofuran. Fraction detection was by means of a Perkin-Elmer LC-25 Refractive Index Detector. The instrument was calibrated using monodisperse samples of polystyrene.

RESULTS AND DISCUSSION

The relationship between bond strength and ageing at 90°C is shown in Figure 1. The breaking strength falls from just under 13 MN m^{-2} to approximately 9 MN m^{-2} . It should be noted that the initial bond strength after 24 h at 25°C is lower than the value found for samples aged for 4 or 8 h at 90°C . This would suggest that there is some post-curing in the initial stages of the thermal treatment.

The variation of the molecular weight of the adhesive polymer with thermal ageing can be seen in Figure 2. An initial increase can be seen followed

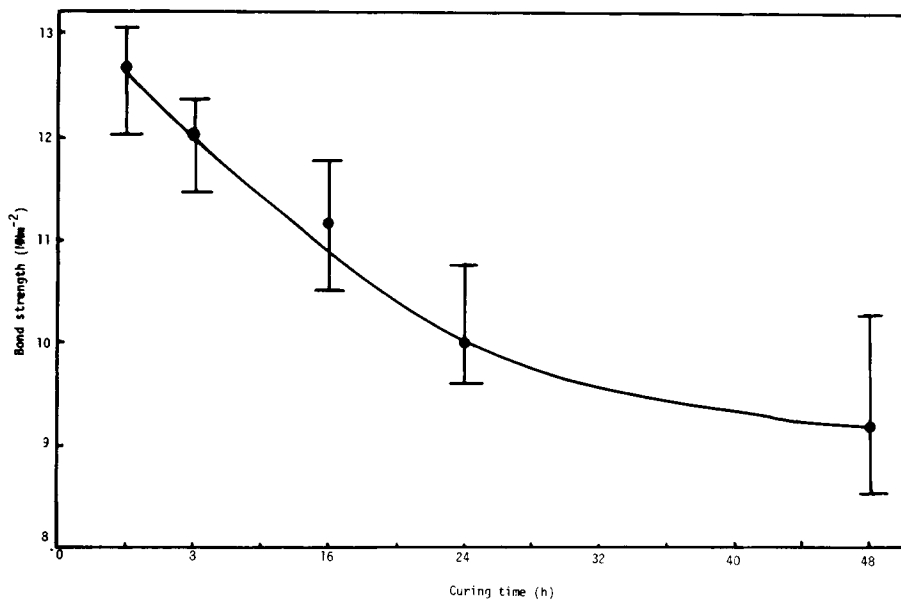


Fig. 1. The effect of ageing at 90°C on the tensile shear strength of poly(ethyl 2-cyanoacrylate) bonded steel-steel joints.

by a slow decrease from 9.24×10^5 to 8.66×10^5 over 48 h. Figure 3 is a typical example of the molecular weight distributions obtained. It should be noted that two peaks are present in the distribution. This makes it impossible to calculate average molecular weights. Values are therefore quoted as the molecular weight corresponding to the distribution maximum. From Figure 2 it can be seen that the molecular weight of the polymer

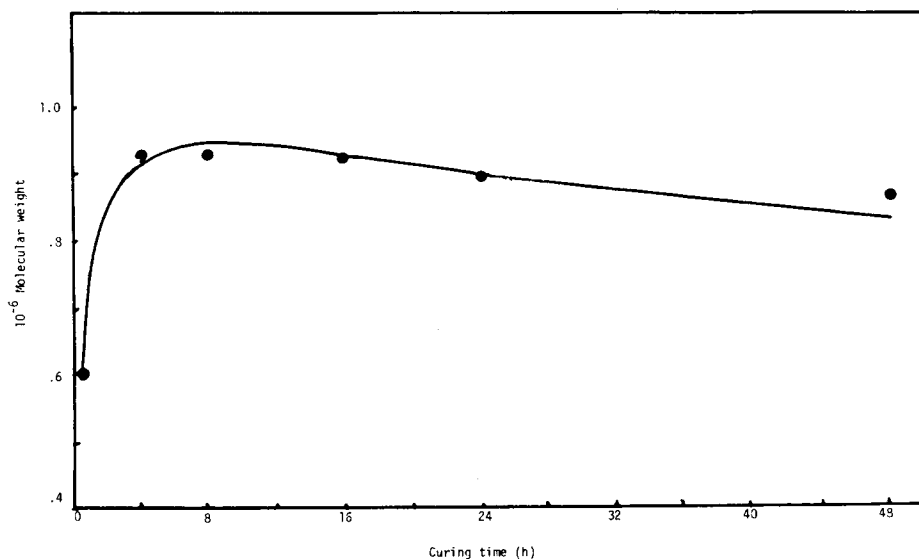


Fig. 2. The effect of ageing at 90°C on the molecular weight of poly(ethyl 2-cyanoacrylate) formed in the glue line of steel-steel joints.

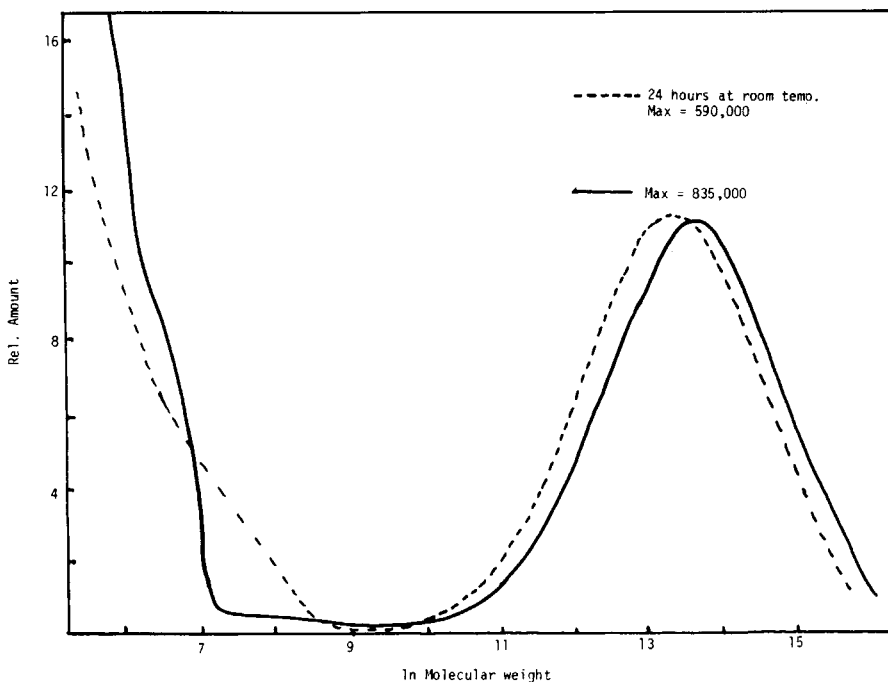


Fig. 3. Molecular weight distribution (polystyrene calibration) of poly(ethyl 2-cyanoacrylate) isolated from steel-steel lap joints (cured for 48 h at 90°C).

formed at room temperature is less than that obtained after 24 h at 90°C. This may be explained if one considers the relative mobilities of the reacting centres at these temperatures. In both cases one would expect the polymerization to be extremely rapid resulting in a rapid increase in the viscosity of the reaction mixture. This is so marked with strongly basic initiators that the reaction ceases rapidly due to the formation of an inert skin over unreacted monomer. In our laboratories polymerizations initiated with triethylamine have remained in this state for several weeks. A comparison of molecular weight distribution, before and after thermal ageing, indicates that monomer is present even after exposure to a post-curing period of 48 h at 90°C. It was unfortunately impossible to ascertain from the GPC traces if the amount of unreacted monomer had increased or decreased during this time. In the case of adhesive bonds this would not be expected to be so marked, but if reactive sites were trapped at 25°C, then one might expect to observe further reaction if the polymer was subjected to ageing at a higher temperature. Prolonged exposure to heat would be expected to result in degradation of the polymer. It is interesting to note that, although the bond strength falls by approximately 30%, the reduction in molecular weight is not particularly dramatic. In fact, after 48 h at 90°C the molecular weight is higher than the initial value after 24 h at room temperature. From these results bond strength does not appear to be closely related to molecular weight. This is not really surprising considering the extremely high values of molar mass involved. The loss in bond strength

could be explained if the polymer undergoes a thermal degradation process similar to that observed for poly(methyl methacrylate) where whole polymer chains "unzip" to produce large amounts of monomer without significant molecular weight loss. If this is the case with poly(ethyl 2-cyanoacrylate), then the monomer produced in the degradation reactions would be trapped in the glue line and give rise to voids and discontinuities that could act as stress concentrators. The production of monomeric material can be seen in the molecular weight distribution in Figure 3. The maximum of the intense peak corresponds to molecular weight of 150. The molecular weight of the monomer is 137. It is difficult to estimate the extent of degradation to monomer as this peak is also observed in samples not subjected to elevated temperatures, presumably due to the presence of unreacted monomer.

CONCLUSION

When steel-steel ethyl 2-cyanoacrylate bonds are subjected to thermal aging at 90°C, there is a marked loss in bond strength. This loss is the net result of an increase due to post-curing and a decrease associated with thermal decomposition. This decomposition is not reflected as a loss in molecular weight. In fact the final molar mass after thermal ageing is greater than the initial value for the unaged material. It is postulated, therefore, that the effect of heat is to depolymerize the polymer by a mechanism similar to that observed with poly(methyl methacrylate). This involves a free radical initiation followed by chain "unzipping" to produce monomer without a significant decrease in molecular weight. The production of monomer is thought to be responsible for disruption of the polymer steel interface and hence a reduction in bond strength. Further studies are being carried out into the mechanism of degradation of poly(ethyl 2-cyanoacrylate).

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