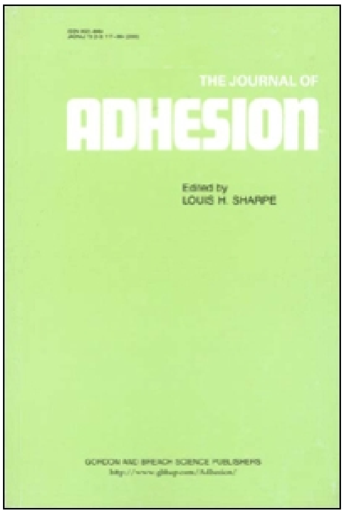

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# Adhesion Studies of Mixtures of Ethyl Cyanoacrylate with a Difunctional Cyanoacrylate Monomer and with other Electron-deficient Olefins

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# Adhesion Studies of Mixtures of Ethyl Cyanoacrylate with a Difunctional Cyanoacrylate Monomer and with other Electron-deficient Olefins*

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Alkyl cyanoacrylate instant adhesives are widely used because of their fast cure speed and versatility on a large number of substrates. Recent performance improvements, such as increased thermal resistance, resulted from the addition of latent acids and polymers, which do not copolymerize with the adhesive monomer, to the adhesive formulations. However, use of these additives can increase fixture time or reduce the final adhesive strength.

Two methods for possibly improving alkyl cyanoacrylate instant adhesives, without loss of cure speed or adhesive properties, could be either crosslinking the alkyl cyanoacrylate monomer with a dicyanoacrylate or copolymerizing it with a second 1,1 disubstituted electron-deficient olefin. A crosslinker, 1,4 butanediol dicyanoacrylate (BDDCA) and two monofunctional monomers, diethyl methylenemalonate (DEMM) and *N,N* diethyl-2-cyanoacrylamide (DECA), were prepared, in good purity, for adhesion studies with ethyl cyanoacrylate (ECA). Crosslinking ECA with BDDCA does improve solvent resistance, as determined by solvent swelling experiments. Glass fixture times are approximately the same for ECA, crosslinked ECA, the pure monomers, and monomer mixtures with ECA, while steel fixture times are generally slower. Crosslinking ECA with BDDCA does not improve lap-shear adhesion, either at room temperature or after thermal exposure at 121°C. Lap-shear strength data, before and after heat exposure, revealed that the ECA/DEMM and the ECA/DECA monomer mixtures exhibit weaker lap-shear adhesive strength than ECA alone.

*Keywords:* Cyanoacrylate; crosslink; instant adhesive; lap-shear adhesive strength; thermal resistance; copolymerization

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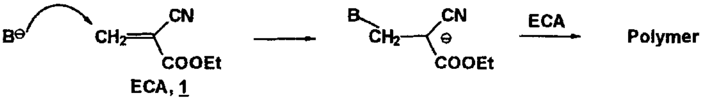
## INTRODUCTION

Alkyl cyanoacrylate instant adhesives are utilized in a wide variety of adhesive applications because of their rapid rate of polymerization and effectiveness on a range of substrates [1]. However, the alkyl cyanoacrylate polymers possess limited thermal stability. To overcome this limitation, latent acids and polymers which possess acidic functional groups have been added to the adhesive formulations to inhibit polymer decomposition [2]. These additives do not copolymerize with the monomer and, as a result, can increase fixture time or reduce final adhesive strength.

The most widely utilized instant adhesive monomer is ethyl cyanoacrylate (ECA), 1. A weak base or nucleophile will readily initiate ECA polymerization. Its reactivity is related to its chemical structure as a 1,1 disubstituted, electron-deficient olefin, *i.e.*, an olefin that contains two electron withdrawing groups on one carbon. This particular chemical architecture makes it an excellent Michael Reaction acceptor for initiation and stabilizes the anionic propagation site during polymerization, as shown in Eq. (1).

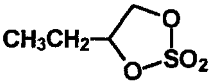


eq. 1

The ECA homopolymer has a 125–150°C ceiling temperature, so that the polymerization is fairly readily reversible [3]. The generally-accepted mechanism for ECA homopolymer thermal decomposition is an "unzipping" of the polymer to free monomer [3], as shown in Scheme I.

SCHEME I

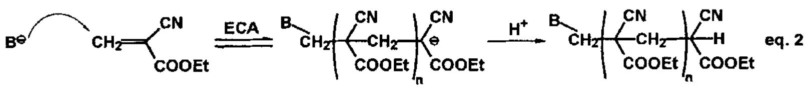
It is believed that inhibiting thermal decomposition would improve the thermal performance of ECA-based adhesives. Previous studies [4] demonstrated that the addition of a latent acid, cyclic sulfate 2, to



**2**

ECA monomer improved steel lap shear adhesion significantly after heating the specimens at 121°C for 48 hours, as shown in Figure 1.

The acid liberated on heating reacts with any anionic polymer end groups and inhibits thermal decomposition, as demonstrated in Eq. (2).



Thermogravimetric analysis (TGA) of the ECA homopolymer with 1% cyclic surfate 2 confirmed this by demonstrating a correlation between the improved lap-shear adhesive strength after heating and the increase in the thermal stability of the modified ECA polymer, as shown in Figure 2.

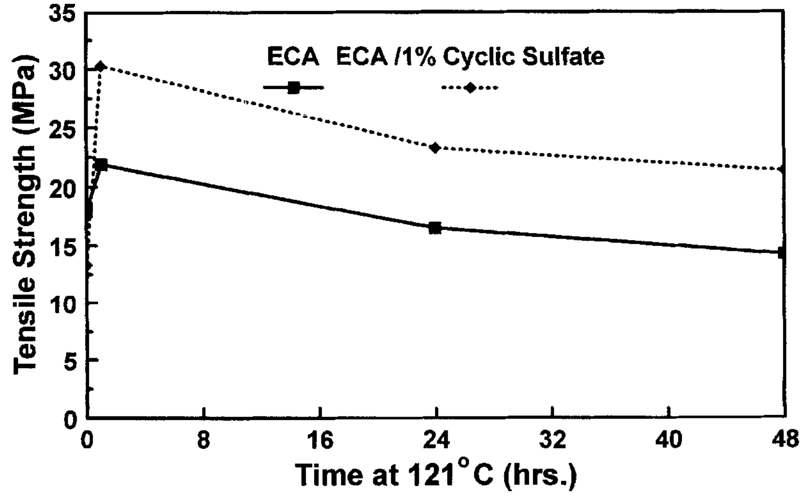


FIGURE 1 Steel lap-shear adhesion of ECA, 1, with and without 2.

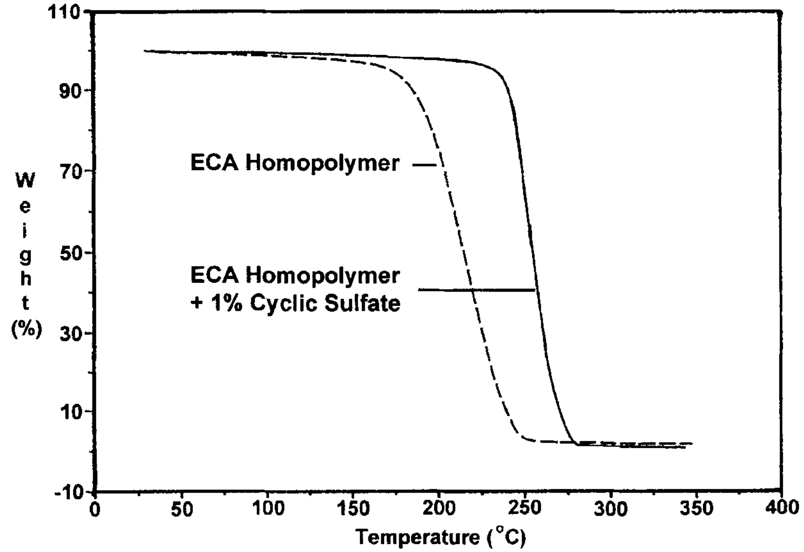
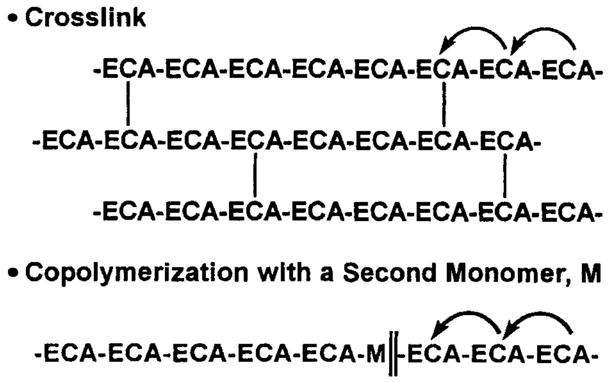


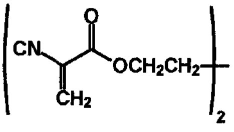
FIGURE 2 TGA analysis of ECA homopolymer with and without cyclic sulfate, 2.

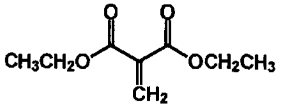
The present study was an attempt to improve the thermal performance of alkyl cyanoacrylate instant adhesives by two different methods to inhibit the "unzipping" that occurs on thermal exposure, as shown in Scheme II. The first method was the addition of a dicyanoacrylate ester crosslinker to ECA, because the mechanical

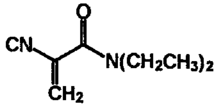


SCHEME II

properties of thermosets are generally unaffected by thermal exposure [5]. The second was the copolymerization of ECA with a second 1,1 disubstituted, electron-deficient olefin, which has a similar chemical architecture to ECA. The crosslinker, butanediol dicyanoacrylate (BDDCA), 3, and the comonomers, diethyl methylenemalonate (DEMM), 4, and *N*,*N* diethyl-2-cyanoacrylamide (DECA), 5, were prepared by a previously-published method [6]. It was shown that the addition of DEMM to ECA increases the thermal stability of the copolymer, as compared with the ECA homopolymer alone [6], as shown by TGA analysis in Figure 3.


BDDCA, 3


DEMM, 4


DECA, 5

The effects of crosslinking ECA with BDDCA on solvent swelling, fixture time, and lap-shear adhesive strength after thermal exposure at 121°C were investigated. The lap-shear adhesive strength of DEMM

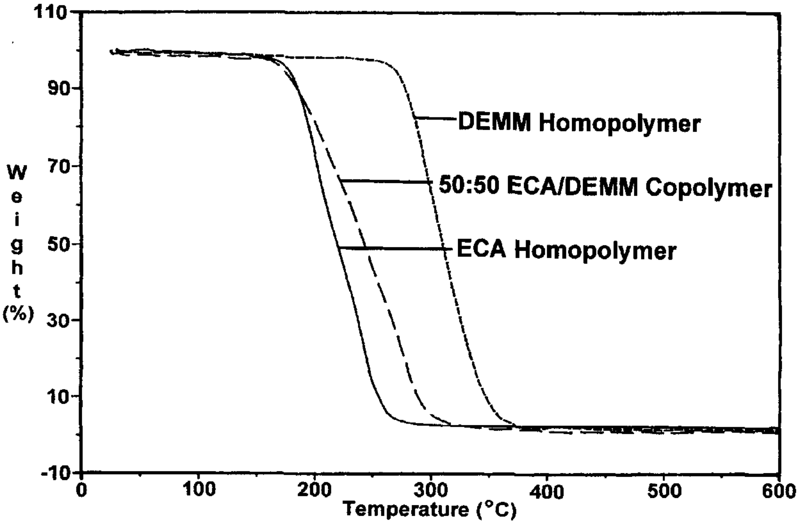


FIGURE 3 TGA analysis of ECA homopolymer, 50:50 ECA/DEMM copolymer, and DEMM homopolymer.

and DECA alone, as well as their mixtures with ECA in model instant adhesive formulations, were also evaluated for their resistance to thermal exposure. Fixture times were also determined.

## EXPERIMENTAL

### Monomer Preparation

Monomers were prepared by a previously-published method [6].

### Solvent Swelling Experiments

Approximately 100 mg of ECA monomer or ECA mixed with 1, 5, 10 and 20 phr of BDDCA was applied as a film to 5 steel lap-shear coupons, and they were exposed to *N*,*N*-dimethyl-*p*-toluidine vapors to effect polymerization. The polymer films were immersed in $CH_2Cl_2$ overnight at room temperature, and the percent solvent swelling was calculated from the weight gain in the polymer film as compared with the weight prior to solvent immersion.

### Fixture Time Procedure

The monomers and monomer mixtures that were utilized in this study are shown in Table I.

#### *Glass*

One drop of monomer or monomer mixture was placed on a glass slide. It was then bonded at a right angle to a second glass slide and

TABLE I Monomers and monomer mixtures

| |
|---|
| ECA, 1 |
| 100:5 ECA, 1/BDDCA, 3 |
| 100:10 ECA, 1/BDDCA, 3 |
| 100:20 ECA, 1/BDDCA, 3 |
| DEMM, 4 |
| 90:10 ECA, 1/DEMM, 4 |
| 50:50 ECA, 1/DEMM, 4 |
| DECA, 5 |
| 90:10 ECA, 1/DECA, 5 |
| 75:25 ECA, 1/DECA, 5 |

held finger tight. Using a series of assemblies, the time was measured until the two slides could not be manually separated.

### *Steel*

Five lap-shear assemblies were bonded with one drop of monomer or monomer mixture with a 1.13 cm overlap and clamped. The bond strength of one of the lapshear assemblies was evaluated at one-minute intervals unit the assembly could not be manually separated. If the lapshears could be manually separated, they were discarded.

### Lapshear Adhesion Tests

The same monomers and monomer mixtures that were used in the fixture time study were also used for the lap-shear tests. Twelve steel lap-shear coupons, grit-blasted on one side, were assembled with one drop of monomer or monomer mixture and clamped. All twelve were aged overnight at room temperature. Three specimens were aged for one hour at 121°C, three for 24 hours at 121°C, and three for 48 hours at 121°C. The remaining three were kept at ambient temperature. After cooling to room temperature the lap-shear assemblies were tested according to ASTM-D1002.

## RESULTS AND DISCUSSION

### Swelling Experiments with Crosslinked ECA

Crosslinking ECA, $\underline{1}$, with BDDCA, $\underline{3}$, should improve solvent resistance. Measuring the amount of polymer swelling that occurs after immersion in solvent is a method for quantifying this effect. ECA was mixed with 1, 5, 10 and 20 phr of BDDCA and polymerized. The polymer films were immersed in $CH_2Cl_2$ overnight at room temperature and the percent swelling was calculated from the weight gain. The results are provided in Figure 4.

The significantly reduced swelling of the crosslinked polymers indicates that solvent resistance of a crosslinked ECA-based adhesive would be improved over ECA alone.

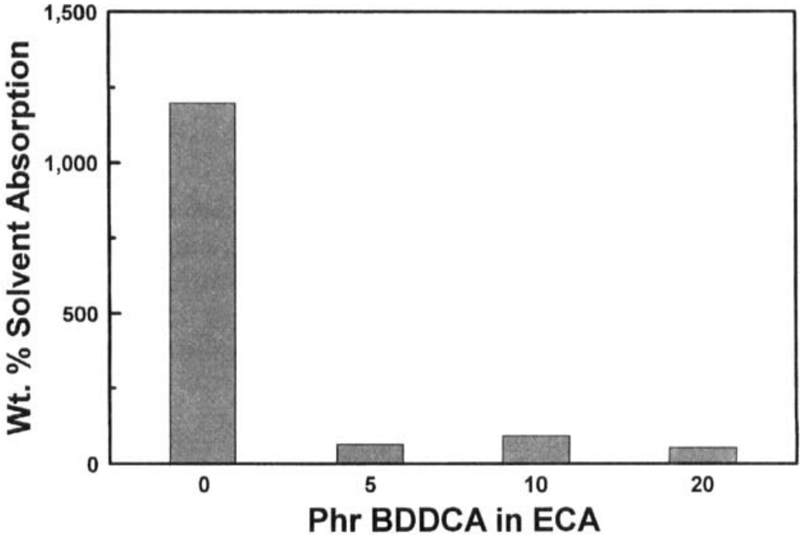


FIGURE 4 Percent swelling of ECA crosslinked with 1, 5, 10, and 20 phr of BDDCA, 3, in $CH_2Cl_2$.

## Fixture Time Tests

Pure ECA, DEMM, DECA, and ECA mixtures with BDDCA, DEMM, and DECA were utilized in fixture time tests on glass and steel. The fixture times on glass and steel are provided in Table II.

All pure monomers and monomer mixtures fixture glass instantly, with the exception of DECA, which requires 60 sec. for glass fixturing

TABLE II Fixture times for pure monomers and monomer mixtures on glass and steel

| *Monomer(s)* | *Glass(sec.)* | *Steel(min.)* |
|---|---|---|
| ECA, 1 | 1 | 1 |
| 100:5 ECA, 1/BDDCA, 3 | 1 | 2 |
| 100:10 ECA, 1/BDDCA, 3 | 1 | 4 |
| 100:20 ECA, 1/BDDCA, 3 | 1 | > 5 |
| DEMM, 4 | 1 | > 5 |
| 90:10 ECA, 1/DEMM, 4 | 1 | 2 |
| 50:50 ECA, 1/DEMM, 4 | 1 | 3 |
| DECA, 5 | 60 | > 5 |
| 90:10 ECA, 1/DECA, 5 | 1 | 2 |
| 75:25 ECA, 1/DECA, 5 | 1 | 1 |

to occur. Glass is a very basic surface and would be expected to initiate the rapid polymerization of these monomers and monomer mixtures, even for the less reactive DEMM and DECA monomers.

The fixture time results on the less basic steel surface are more complicated. As the level of BDDCA increases in ECA, fixture times unexpectedly increase. Because BDDCA is extremely reactive, it may more rapidly increase adhesive viscosity, thereby hindering diffusion and increasing the overall fixture time.

As the concentration of DEMM in ECA increases, steel fixture times increase. This is not unexpected, because the rate of DEMM polymerization is so much slower than ECA [6].

Steel fixture times actually improve as increasing levels of DECA are added to ECA, although fixture time for pure DECA is very slow. As was previously demonstrated [6], adding DECA to ECA actually initiates polymerization. This reactivity will cause the ECA/DECA blend to fixture more quickly than otherwise might be expected. The 75:25 ECA/DECA mixture did have a barely sufficient pot-life for lap-shear assembly, while the 50:50 mixture did not. This is the reason why the ECA/DECA adhesion experiments were performed with a 75:25 monomer ratio instead of the 50:50 mixture employed in the ECA/DEMM study.

## Lapshear Adhesion Tests after Thermal Exposure

Steel lap-shear adhesive strength was measured after aging the specimens at room temperature and at 121°C for 1, 24, and 48 hours, respectively. Lap-shear specimens, which were aged at ambient temperature, were utilized as controls. The steel lap-shear adhesive strengths of ECA, 1, crosslinked with BDDCA, 3, before and after thermal aging, are shown in Figure 5.

Crosslinking ECA with BDDCA does not improve lap-shear adhesive strength after heating at 121°C for 48 hours, as compared with ECA alone. At the 10 and 20 phr levels, the crosslinking actually reduces lap-shear adhesive strength, possibly through increased embrittlement of the polymer matrix. However, polymer "unzipping" is apparently still very facile, despite the presence of the crosslinks.

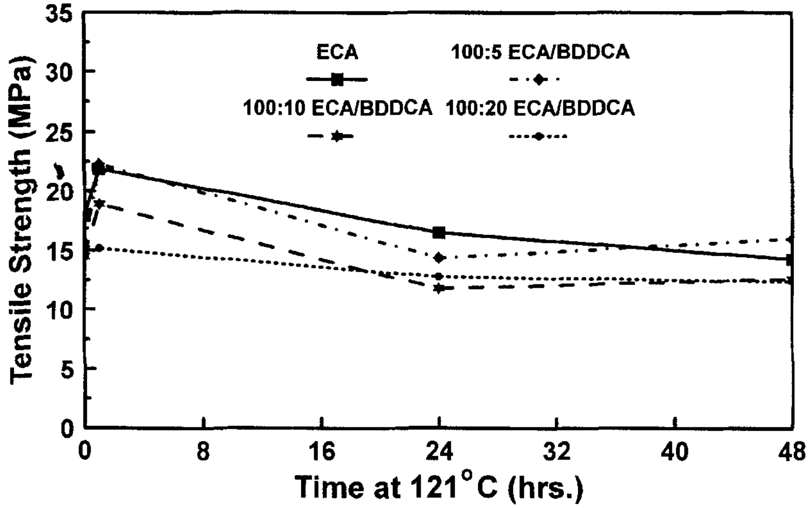


FIGURE 5 Lap-shear adhesion data for ECA, 1, and ECA crosslinked with 5, 10, and 20 phr of BDDCA, 3.

The steel lap-shear adhesive strengths of ECA, 1, mixed with DEMM, 4, before and after thermal aging, are shown in Figure 6.

DEMM addition to ECA reduces initial lap-shear adhesion, but, while the adhesion is weak for the 50:50 ECA/DEMM mixture, there is no loss of strength after heating at 121°C for 48 hours. No adhesive strength data were collected for pure DEMM because it evaporated from the bondline within 5 hours at room temperature, before an adhesive bond could form. The lap-shear adhesive strength of ECA decreases after heating at 121°C for 48 hours. In contrast, the 50:50 ECA/DEMM lap-shear adhesive strength increases, at first, and does not decrease after heating at 121°C for 48 hours, although this mixture still exhibits a lower initial and final adhesive strength, as compared with ECA.

The steel lap-shear adhesive strengths of ECA, 1, mixed with DECA, 5, before and after thermal aging, are shown in Figure 7.

The final lap-shear adhesive strengths, after heating the specimens at 121°C for 48 hours, are all significantly lower than those for ECA alone. The addition of DECA to ECA does not improve the thermal stability of the ECA adhesive.

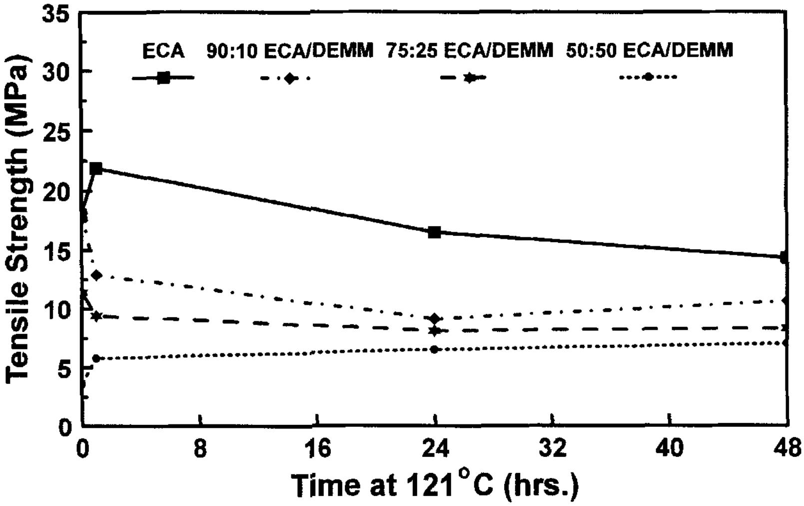


FIGURE 6 Lap-shear adhesion data for ECA, 90:10 ECA/DEMM, 75:25 ECA/DEMM, and 50:50 ECA/DEMM.

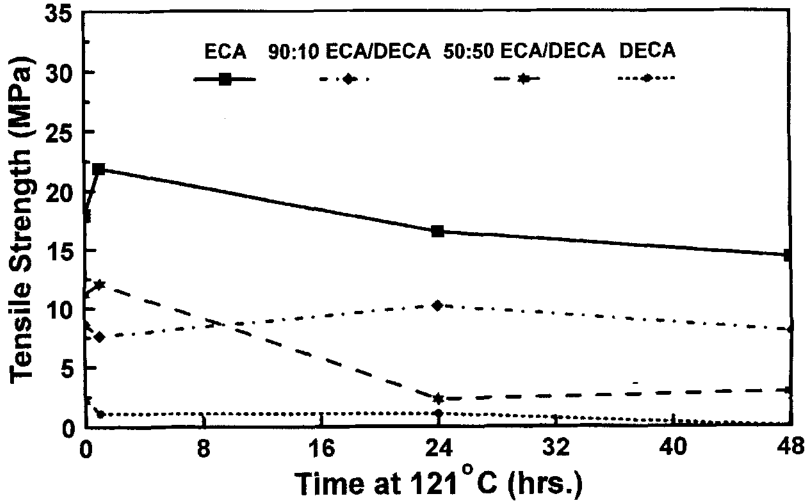


FIGURE 7 Lap-shear adhesion data for ECA, 90:10 ECA/DECA, 75:25 ECA/DECA, and DECA.

From these adhesion experiments, a ranking can be estimated for the usefulness of the three monomers. ECA, 1 is clearly the most adhesive-effective monomer, as compared with DEMM, 4 and DECA, 5. This is not surprising because ECA is more reactive toward anionic polymerization and produces a homopolymer with a higher degree of polymerization than DEMM or DECA [6]. Also, the generally-accepted order of electron withdrawing capability of the different substituents [7] on the olefins utilized in this study is shown below.

$$—CN > —COOR > —CONEt_2$$

The combination of the CN and COOR groups on ECA is more strongly electron withdrawing than the combination of substituents on either DEMM or DECA. The stronger electron withdrawing groups create a more highly polarized double bond, making ECA more reactive toward the Michael-type addition initiation and subsequent polymerization than DEMM or DECA to form an effective adhesive bond.

## CONCLUSIONS

Crosslinking ECA, 1, with BDDCA, 3, would improve the solvent resistance of ECA-based instant adhesives in bonding applications. However, the addition of a crosslinker to ECA failed to provide the expected improvement in the thermal properties of the ECA adhesive, and it had little or no effect on glass or steel fixture times or lap-shear adhesive strength. The presence of any linear, terminal ECA polymer segments in the polymer network must initiate the “unzipping” of the crosslinked polymer as readily as for the ECA homopolymer alone. Since the crosslinks have the same basic chemical bond structure as that of the ECA homopolymer, they must have a similar chemical reactivity as well. On thermal exposure, the crosslinked polymer still reacts in the same manner as the linear ECA homopolymer and “unzips” to yield free monomer at relatively low temperatures, as shown in Scheme III. This was confirmed by thermogravimetric analysis (TGA) of crosslinked ECA polymer, which was prepared and

SCHEME III

isolated in a separate study [6]. Therefore, because of the relatively low ceiling temperature of alkyl cyanoacrylate polymers, the advantages in the thermal stability of thermosets were unrealized.

While earlier studies demonstrated that the 50:50 ECA/DEMM copolymer possesses improved thermal stability over the ECA homopolymer [6], this fact did not provide improved lap-shear adhesive strength after thermal exposure for the same monomer mixture. Glass fixture times are unaffected by DEMM, 4 or DECA, 5, addition to ECA, but steel fixture times increase, and lapshear adhesive strength is reduced, even before thermal exposure. This decrease in initial adhesive strength may be attributed to the reduction in the molecular weight of the adhesive copolymer, as compared with the ECA homopolymer, described earlier [6], or by a decrease in the effective interaction of the adhesive polymer with the substrate surface. Even if the adhesive polymer decomposition is inhibited by the presence of a comonomer, this physical property advantage of the polymer cannot overcome the decrease in the initial lap-shear adhesive strength. The addition of a second electron-deficient monomer to ECA did not provide the expected improvement in the thermal performance of ECA-based instant adhesives.

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## References

[1] Coover, H. W., Dreifus, D. W. and O'Connor, J. T., *Handbook of Adhesives*, 3rd edition, Skeist, I., Ed. (Van Nostrand Reinhold, NY, 1990), p. 463.
[2] O'Connor, J. T., *Chem. Tech.*, Sept. 1994, p. 51.

[3] Winkler, B. and Miyaji, W., *Cyanoacrylate Resins – the Instant Adhesives*, Lee, H., Ed. (Pasadena Technology Press, Los Angeles, 1986), p. 9.
[4] Attarwala, S. and Klemarczyk, P., U. S. Patent 5,328,944 (1994).
[5] Hiemenz, P., *Polymer Chemistry, the Basic Concepts* (Marcel Dekker, Inc., New York, 1984), p. 314.
[6] Klemarczyk, P., *Polymer* **39**(1), 173 (1998).
[7] Perlmutter, P., *Conjugate Addition Reactions in Organic Synthesis* (Elsevier, New York, 1992), p. 5.