Thermal Behaviour and Adhesive Properties of Some Cyanoacrylate Adhesives with Increased Heat Resistance

Z. Z. DENCHEV* and V. S. KABAIVANOV

Scientific Research Center for Speciality Polymers, 4A Kliment Ohridsky Street, 1756 Sofia, Bulgaria

SYNOPSIS

Cured adhesive layers produced from ethyl-(ECA), allyl-(ACA), and allyloxyethyl-(AOECA) 2-cyanoacrylates were studied by means of thermogravimetry and differential scanning calorimetry. Polymer films of ECA-based adhesive compositions comprising various amounts and types of 2-cyano-2,4-pentadienoic acid (CPDA) esters were also examined. The influence of the modifier type, as well as the chemical structure of the cyanoacrylates used, was followed upon the glass transition temperatures (T_g) and the rates of thermal degradation of the corresponding polymers. In the case of cured adhesive mixtures containing unsaturated CPDA esters and when poly(ACA) and poly(AOECA) were studied, a significant increase of their heat resistance was established, as compared with poly(ECA). This fact was explained with the formation of three-dimensional structure of the polymer film due to crosslinking reactions. A different course and character of these reactions were found comparing the thermal behavior of poly(ACA) and cured compositions containing unsaturated CPDA esters. A good agreement was found between data from the thermal analyses and the tensile shear and impact strength tests. It was shown that the modification of ECA with unsaturated CPDA esters is a possible way of increasing the heat resistance of the basic adhesive. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Cyanoacrylates, which could be classified as specialty structural adhesives, are known to be useful in bonding operations involving a variety of substrates. These adhesives require no heat, pressure, or addition of catalysts to cure. They polymerize rapidly at room temperature when exposed to minor amounts of moisture, typically found on the substrates being bonded.[1]

Unfortunately, the cyanoacrylates of industrial use have their limitations, the most important of them being that the adhesive bond, once cured, exhibits decreased performance at raised temperatures (above 80°C). This fact could easily be explained in terms of the structure of the adhesive layer formed, containing quaternary C atoms in the main chain. This polymer type is known to have a low resistance to heat due to its inclination to depolymerize rapidly at mild temperatures.[2]

It is of practical interest to overcome, at least to some degree, this disadvantage to increase the versatility of the cyanoacrylate adhesives.

There are several general ways to increase the heat resistance of polymers.[3] As regards cyanoacrylate adhesives, the only possible way toward increased heat resistance is the formation of crosslinks in the adhesive layer, thereby reducing its ability to depolymerize. So far, two different methods have been described to the purpose, one of them being the preparation of unsaturated esters of 2-cyanoacrylic acid $CH_2 = C(CN)COOR$, e.g., allyl-(ACA),[4] propargyl-(APA),[5] and more recently allyloxyethyl-2-cyanoacrylate-(AOECA).[6] On the other hand, the modification of industrial cyanoacrylates [mostly ethyl-2-cyanoacrylate(ECA)] by addition of various types of polymerizable bifunctional monomers has also been applied with good results. Compounds that have been tried to this purpose are some methacrylates and dimethacrylates,[7,8] fluorinated monomers containing double and triple bonds,[9] etc.

An effort in developing new monomers with the application as ECA heat resistance promoters is the use of alkyl esters of 2-cyano-2,4-pentadienoic acid (CPDA). Adhesive mixtures prepared thereof with ECA are said to exhibit increased resistance to heat, as compared with the basic ECA itself.[10,11]

Recently, some new monomeric cyanopentadienoate esters of the general formula (1) have been synthesized and characterized[12]:

$$CH_2=CH-CH=C \begin{array}{c} CN \\ \diagup \\ \diagdown \\ C(O)-O(CH_2CH_2O)_n-R_1 \end{array}$$

$$(1)$$
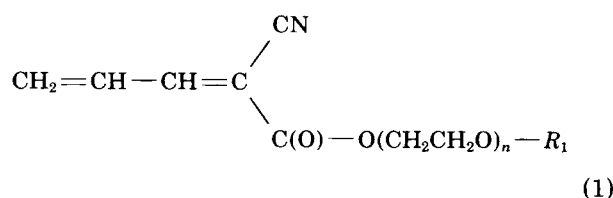
where if R_1 = alkyl $(C_{1,2,4})$ n = 2 and if R_1 = allyl n = 0, 1, 2.

It is an aim of the present work to study the thermal behavior of polymer films from various pure adhesives and adhesive mixtures, these films being prepared under the conditions of adhesive bond formation. The obtained results are used to explain the differences in the bonded joint performance after heat treatment of the junctions raised up to 150°C temperatures.

EXPERIMENTAL

With the exception of ECA, a product commercially available as Kanokonlit-E, all cyanoacrylate monomers used were synthesized from the corresponding cyanoacetates and paraformaldehyde in a manner well known by art.[13] The CPDA esters were prepared by a published method, too.[14]

The adhesive compositions were produced by admixing of proper quantities of the corresponding CPDA ester to the ECA monomer at room temperature. In that way, colorless and homogeneous adhesive mixtures were obtained and afterward used for bonding of standard joints.

Tensile shear strength was determined on overlapping specimens made of steel (0.2% C content) on a Zwick-1474 testing machine at 20°C in accordance with ASTM D1002 and a constant crosshead speed of 50 mm/min. The substrates for this determination were slightly roughened with extrafine sandpaper and degreased with acetone. They were used without further activation or chemical treatment of the adhered surfaces.

Impact strength was determined according to ASTM 950-72. Surface preparation of the specimens was the same as described above.

Each of the reported values in the strength tests represents the average of 10–15 experiments.

The thermal ageing of the junctions was performed after 24 h had passed from joint formation. Prior to failure of the bonded joints, the adhered specimens were allowed to return to room temperature in a dessicator.

The calorimetric investigations were performed on a Perkin-Elmer differential Scanning calorimetry (DSC)-2C apparatus at 10°/min scanning rate. For the thermogravimetric (TG) studies, a Perkin-Elmer TG-2 balance was used. In all cases, the studied polymer samples were the adhesive layers removed from the specimens with a sharp blade after failure of the junction.

RESULTS AND DISCUSSION

Thermal Analyses of Cured Adhesive Layers

To conclude in what way and to what extent the adhesive bond strength at raised temperatures is associated with the thermal behavior of the corresponding cured adhesive, DSC and TG investigations were performed. On the one hand, we studied poly(ACA) and poly(AOECA) in comparison with poly(ECA) samples. On the other hand, the differences in the performance of cured adhesive mixtures containing CPDA esters and that of the basic ECA adhesive were also pointed out.

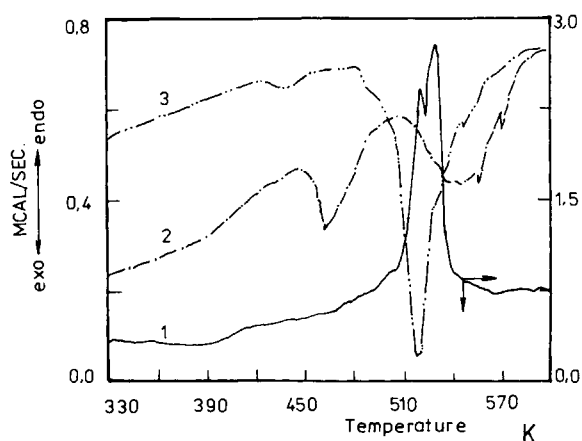As apparent from Figure 1, the DSC curves of

Figure 1 DSC curves of poly(2-cyanoacrylate) layers. Conditions: scanning rate, 10°/min; initial sample weight, 3–5mg. (1) poly(ECA), (2) poly(ACA), (3) poly(AOECA).

Table I Glass Transition Temperatures of Poly(Cyanoacrylates):

$$\begin{array}{c} CN \\ | \\ (-C-CH_2-)_x \\ | \\ C(O)-O(CH_2CH_2O)_n-R \end{array}$$

Polymer Type	$T_g(°C)^a$	Transition Interval (°C)
R = ethyl, n = 0; poly(ECA)	132.9	21.1
R = allyl, n = 0; poly(ACA)	119.7	20.0
R = n-propyl, n = 0	103.9	22.5
R = allyl, n = 1; poly(AOECA)	21.1	18.3
R = n-pentyl, n = 0	93.8	23.0

[a] All T_g values were registered during the second scan after entire polymerization of the samples.

poly(ACA) (2) and poly(AOECA) (3) showed exothermal peaks at 235–314°C and 250–308°C, respectively, thereby having supported the supposition for crosslink formation in these cases. At the same time, poly(ECA) (1) exhibited an endothermal peak of intensive depolymerization in the 225–280°C temperature range. Also, it is important to mention that the formation of the three-dimensional structure in the poly(ACA) layer started at a temperature 35°C higher than that of the poly(AOECA) sample.

In curves 2 and 3, there were more slightly expressed exothermal peaks at 167–234°C (2) and 150–190°C (3), which should be ascribed to the final polymerization of certain amounts of the corresponding monomers. That was not the case for poly(ECA) (1). In that sample, no measurable monomer amounts were found. This different performance of the studied homopoly(cyanoacrylates) is attributable to the variable quantities of inhibitors (SO_2 and hydroquinone) (see the notes to Table III), which are usually introduced into the monomeric adhesives in the process of their preparation.

In Table I, the T_g values of the studied homocyanoacrylate polymers are compared.

As expected, it was found that T_g strongly depended upon the chemical composition of the polymers. A trend of T_g reduction was established when the size of R was varied from $-C_2H_5$ to $-CH_2CH_2OCH_2CH=CH_2$. Most probably, this was due to a disimprovement of the main chains' spacial arrangement. As obvious from Table I, the allyl moiety of poly(ACA) caused a higher rigidity of the structure compared with the alkyl group with the same number of C atoms, e.g., n-propyl. When there was an ether atom in the side chain, T_g abruptly dropped. That was ascribed to an intensification of the internal rotation in the polymer

chains. Probably for this reason, poly(n-pentyl-2-cyanoacrylate), containing the same number of C atoms in its ester radical as that of poly(AOECA), had a T_g considerably higher than that of poly(AOECA).

In each of the cases represented in Table I, only one T_g value was registered, the temperature intervals of transition being relatively narrow and of one and the same order.

Our further experiments involved TG investigations. Figure 2 depicts the thermal degradation curves of the studied cured cyanoacrylate adhesives at linear increase of the temperature in an inert atmosphere. Poly(ECA) samples (1) started losing weight at about 170°C. In the 200–210°C range, this process ran at maximum rate. As regards poly(ACA) (2) and poly(AOECA) (3), their destruction was strongly impeded, the carbonized residues at 530°C having been larger than that of poly(ECA). These

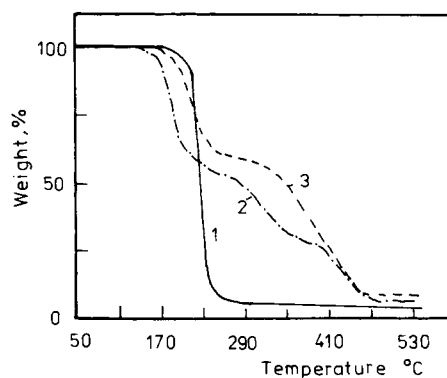**Figure 2** TG curves of poly(2-cyanoacrylate) layers. Conditions: scanning rate, 10°/min; initial sample weight, 30–40 mg. (1) poly(ECA), (2) poly(ACA), (3) poly(AOECA).
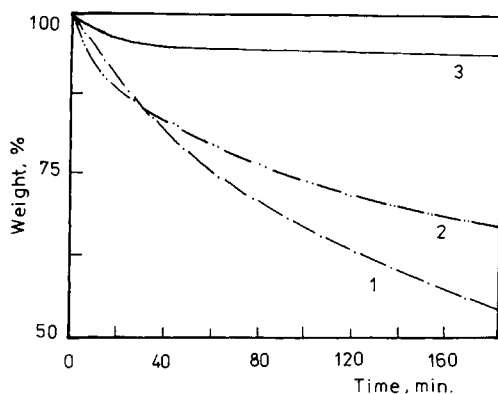
Figure 3 TG curves of poly(2-cyanoacrylate) layers. Conditions: isothermal mode (3 h/140°C); initial sample weight, 30–40 mg. (1) poly(ECA), (2) poly(ACA), (3) poly(AOECA).

results could be explained in terms of crosslinking, caused by the reaction of the pendant allyl groups, as pointed out in earlier studies.[15]

Figure 3 shows the curves of thermodestruction of cured ECA, ACA, and AOECA, registered in an inert atmosphere under isothermal conditions, most similar to those of the adhesive bonded joint aging. The depropagation of poly(ECA) (1) proceeded vigorously and relationship followed a nearly exponential course, reaching the final value of 45% weight loss. Surprisingly, the rate of thermal destruction of poly(ACA) (2) was found to be higher than that of poly(ECA) until the 40th minute of the TG test. Afterward, it was strongly impeded, but, nevertheless, the weight loss at the end of the test was significant—32%.

The poly(AOECA) sample (3) was found to have a different performance. Until the 40th minute, it loses only about 3% of its weight. A further weight

loss was not registered. Most probably, the particularities of the AOECA structural unit, already mentioned above, allowed the formation of the three-dimensional structure at lower temperatures and in a higher degree as compared with poly(ECA).

Interesting changes of the thermal properties were established when cured ECA-based adhesive mixtures were studied containing CPDA esters. Table II shows a well-pronounced trend of T_g diminution for polymer samples including equal amounts of various dienoates. Having in mind our earlier IR spectral investigations concerning the homopolymerization of CPDA esters,[16] the above-mentioned effect was ascribed to possible incorporation of 1,4-*trans* and 1,4-*cis* units from the corresponding dienoate compound into the polymer chain. The presence of a π-electron bond in the main chain in immediate vicinity of a σ-bond, about which rotation could be realized, strongly lowers the potential barrier of this process, i.e., favors a flexibility increase. Apart from this, the influence of the side chains' composition should also be taken into consideration when discussing the T_g decrease.

From Table II is also apparent that the CPDA-containing polymerized adhesive mixtures displayed considerably expanded transition intervals, as compared with homopoly(cyanoacrylates). This could be explained by the structure of the modified poly(ECA) adhesive layer, obviously containing relatively large microsections of different composition.

Figure 4 depicts the results from TG analyses of cured mixed adhesives carried out at linear temperature increase. Studying the weight loss as a function of the temperature, a similar course of all curves was established. The thermal decomposition of the unmodified poly(ECA) sample (1) started at 175°C,

Table II **Glass Transition Temperatures of Cured ECA-Based Adhesive Mixtures Including CPDA Modifiers:**

$$
\begin{array}{c}
CN \\
| \\
(-C-CH{=}CH-CH_2-)_x \\
| \\
C(O)-O(CH_2CH_2O)_n-R_1
\end{array}
$$

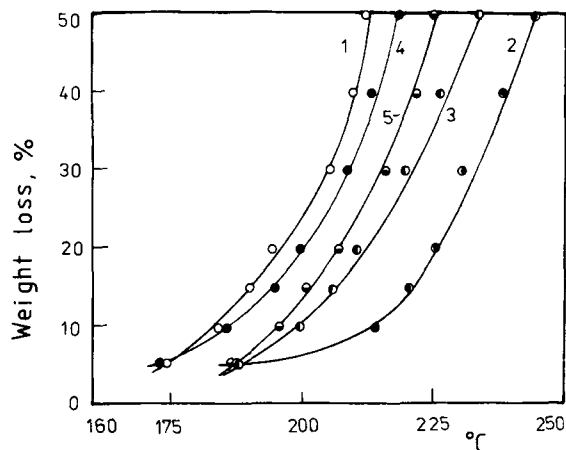| Type of Dienoate Modifier	Content (mol %)	$T_g(°C)^a$	Transition Interval (°C)
—	—	132.9	21.1
R_1 = ethlyl, n = 0; (ECPD)	10	106.7	40.0
R_1 = allyl, n = 0; (ACPD)	10	95.5	40.0
R_1 = allyl, n = 1; (AOECPD)	10	64.5	44.0
R_1 = allyl, n = 2; (AOEECPD)	10	47.6	49.5

[a] See the note to Table I.
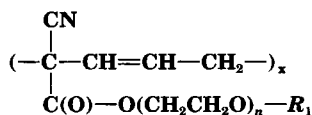
Figure 4 Weight loss vs. temperature for polymerized ECA-based adhesive mixtures, each sample containing 10 mol % of various CPDA esters: (1) no modifier, (2) ACPD, (3) AOECPD, (4) AOEECPD; (5) ECPD. Conditions: heating rate, 10°/min; initial sample weight, 35–45 mg.

Figure 5 Weight loss vs. temperature for polymer adhesive layers. Conditions: heating rate, 10°/min; initial sample weight, 35–45 mg. (1) poly(ECA), (2) poly(ACA), (3) poly(AOECA), (4) poly(ECA + 10 mol % ACPD).

the 50% weight loss having been registered at 213°C. In all other cases of modified ECA samples (curves 2–5), higher temperatures of initial and half decomposition were found, most distinctly expressed in curve 2 (ACPD modification). There, the 5 and 50% weight losses were registered at 187 and 245°C, respectively, i.e., a higher heat resistance of the samples was revealed. This was ascribed to the formation of the three-dimensional structure. There was sufficient reason to make that supposition, having in mind the inclination of unsaturated polymeric CPDA esters to get crosslinked even at room temperature.[16] Similar behavior had been registered for the saturated dienoate esters, but only at increased (up to 110°C) temperatures.

Our experiments showed that the thermal behavior of cured adhesives comprising cyanopentadienoates, on the one hand, and of poly(ACA) and poly(AOECA), on the other hand, were similar to a great extent. In both cases, the increased heat resistance of the studied polymers seemed connected with a crosslink formation in the adhesive layer. The course of the curves in Figure 5, however, required a special explanation. It allowed the conclusion that there were important differences between the kind of thermal degradation of these two adhesive types. Curves 1 and 4 characterizing poly(ECA) and the polymerized mixture of ECA with 10 mol % ACPD had one and the same course. Above 10% of weight loss, they were displaced from each other with about 35°C. The thermodestruction of poly(ACA) and poly(AOECA) were characterized by curves, which changed their slopes above 40 and 30% of weight
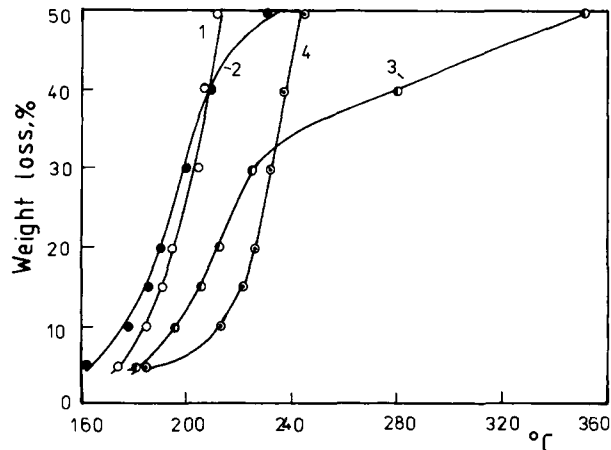
loss, respectively. Afterward, a strong diminution of the losses was registered. On this basis, we presumed that during the thermal treatment of samples produced from monomeric mixtures comprising unsaturated CPDA esters the building of crosslinked layer structures ran at temperatures lower than 160°C (10°/min heating rate). Under these conditions, measurable thermodegradation did not proceed. That was not the case for poly(ACA) and poly(AOECA) samples. There, the crosslink formation and thermodestruction obviously ran as rival processes, the former taking effect after a considerable weight loss.

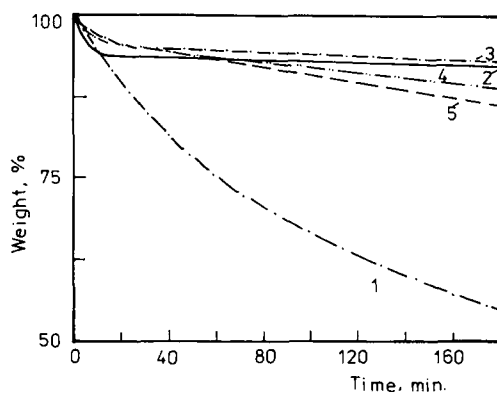Figure 6 shows that all polymers produced from ECA by its modification with unsaturated CPDA

Figure 6 TG curves (isothermal mode, 3 h/140°C) of polymerized ECA-based adhesive mixtures, each sample containing 10 mol % of: (1) no modifier, (2) ACPD, (3) AOECPD, (4) AOEECPD, (5) ECPD.

esters exhibit better performance during the iso-thermal test, as compared with the basic monomer. The weight losses were in the 8–12 wt % range, vs. 45% for homopoly(ECA).

Adhesive Properties of Metal Joints, Bonded with Pure and Modified Cyanoacrylates

In Table III, the tensile shear strength values of all studied adhesives were compared after aging of the bonded joints at three different temperatures.

As apparent, when pure AOECA or ACA were applied relatively low σ_s^{init} values were registered, as compared with unmodified ECA. Observation of the failure mode of the tested bonds showed mainly cohesive failure at room temperature for all three pure adhesives. The low observed σ_s^{init} of ACA adhesive could be explained by the presence of unpolymerized monomer (see Fig. 1). The initial bond strength of AOECA of only 7.0 MPa may be explained in terms of the low T_g of the corresponding polymer and its low cohesive strength.

The failure of the junctions, thermally treated at 100°C for 24 h, however, yielded evidence that ACA provides significantly more stable adhesive bonds. Superior performance of AOECA-bonded details after aging for 5 h at 150°C was found out, which was in a good agreement with the TG analyses of homo-poly(cyanoacrylates), already mentioned above (Figs. 2 and 3).

The modification of ECA with various CPDA esters, as a rule, resulted in higher σ_s^{init} values in comparison with those of the basic adhesive. This was expressed to different extents depending upon the type and concentration of the modifiers. When unsaturated CPDA esters were used, the concentrations required to achieve the optimum tensile shear strength were lower than that of the saturated dienoates applied.

The thermal treatment of the junctions at 100°C showed clearly that only the unsaturated dienoate modifiers were suitable as heat resistance promoters. This tendency was even more distinctly expressed when σ_s^{150} values were compared. We supposed that with the increase of the number of O atoms in the modifier's ester radical a "softer" polymer layer was created in which the chains had a larger set of conformations. Thus, the increase of internal strain and embrittlement during the final polymerization and especially during the crosslinking of the layer was obviously restricted.

It was also found that the use of saturated dienoic modifiers caused σ_s^{100} and σ_s^{150} values close to those of the basic ECA. This effect could be explained by the above-mentioned considerably lesser ability of the saturated poly(CPDA) esters to form cross-

Table III Tensile Shear Strength (σ_s) of Steel Joints with Various Cyanoacrylate Adhesives and Adhesive Compositions

No.	Basic CA Monomer	Modifier Type (content,[a] wt %)	Tensile Shear Strength (MPa)		
			23°C/24 h (σ_s^{init})	100°C/24 h (σ_s^{100})	150°C/5 h (σ_s^{150})
1	ECA[b]	—	16.6 ± 1.8	12.2 ± 2.0	3.2 ± 0.6
2	ACA[c]	—	12.7 ± 1.9	29.1 ± 1.8	3.2 ± 0.5
3	AOECA[d]	—	7.0 ± 1.0	14.3 ± 1.0	7.8 ± 1.5
4	ECA	ACPD (5)	20.2 ± 2.0	27.8 ± 2.9	4.3 ± 0.3
5	ECA	AOECPD (3)	20.5 ± 1.4	24.3 ± 3.0	8.7 ± 0.7
6	ECA	AOEECPD (3)	21.4 ± 1.2	25.5 ± 1.0	10.0 ± 1.2
7	ECA	MCPD (10)	26.5 ± 2.0	16.2 ± 2.0	3.6 ± 1.2
8	ECA	ECPD (10)	20.8 ± 1.3	15.6 ± 1.0	3.8 ± 1.0
9	ECA	BCPD (20)	20.3 ± 1.0	14.2 ± 1.0	2.4 ± 0.7
10	ECA	MEECPD (10)	18.7 ± 1.8	14.0 ± 1.6	2.4 ± 0.8
11	ECA	EEECPD (10)	22.6 ± 2.0	16.0 ± 1.5	2.3 ± 0.8
12	ECA	BEECPD (10)	22.0 ± 1.8	13.0 ± 1.8	2.1 ± 0.3

[a] The CPDA ester content was varied within the range of 0.5–50 wt % (in respect to ECA) and only those compositions were included, displaying the optimum strengths at the three studied temperatures.

[b] Content of inhibitors: SO_2, 35 ppm; hydroquinone, 180 ppm.

[c] Content of inhibitors: SO_2, 140 ppm; hydroquinone, 540 ppm.

[d] Content of inhibitors: SO_2, 80 ppm; hydroquinone, 2400 ppm.

MCPD: $n = 0$, R_1 = methyl. BCPD: $n = 0$, $R_1 = n$ butyl. MEECPD: $n = 2$, R_1 = methyl. EEECPD: $n = 2$, R_1 = ethyl. BEECPD: $n = 2$, $R_1 = n$-butyl.

Table IV   Impact Strength of Steel Joints Bonded with Various Cyanoacrylate Adhesives and Adhesive Compositions

No.	Basic CA Monomer	Modifier Type (content,[a] wt %)	Impact Strength (kJ/m^2)		
			23°C/24 h	100°C/24 h	150°C/5 h
1	ECA	—	4.8 ± 0.3	2.2 ± 0.3	1.2 ± 0.3
2	ACA	—	5.9 ± 0.7	3.8 ± 0.5	1.6 ± 0.3
3	AOECA	—	5.5 ± 0.7	3.8 ± 0.3	2.4 ± 0.5
4	ECA	ACPD (5)	7.0 ± 0.3	2.8 ± 0.3	1.4 ± 0.1
5	ECA	AOECPD (5)	7.1 ± 0.5	2.1 ± 0.1	1.4 ± 0.1
6	ECA	AOEECPD (3)	6.8 ± 0.7	2.5 ± 0.2	2.0 ± 0.2
7	ECA	MCPD (10)	7.9 ± 0.5	2.0 ± 0.1	1.6 ± 0.3
8	ECA	ECPD (20)	8.5 ± 0.6	3.2 ± 0.3	1.9 ± 0.6
9	ECA	MEECPD (5)	6.5 ± 0.3	2.3 ± 0.1	1.2 ± 0.1
10	ECA	EEECPD (20)	5.6 ± 0.8	2.0 ± 0.1	1.6 ± 0.1
11	ECA	BEECPD (10)	6.0 ± 0.5	2.1 ± 0.1	1.4 ± 0.2

[a] See the notes to Table III.

linked structures. Therefore, an insufficient degree of crosslinking was to be expected in the corresponding polymerized adhesive mixtures after heat treatment. That would have as a result a lower heat resistance of the joints bonded with these mixed adhesives. The data in Table III are in good agreement with this supposition.

The thermal treatment of ECA bonds changed the failure mode from cohesive to adhesive (interfacial). The presence of crosslinkable cyanoacrylate monomer or unsaturated dienoate modifier, however, always gave a cohesive failure mode, even when the polymer bond line showed signs of degradation and brittleness.

The results from the impact testing are shown in Table IV. They were in good agreement with the tensile shear strength data and with the proposed explanation of these data. The adhesive compositions containing proper amounts of CPDA esters exhibit better impact properties as compared with the pure basic adhesive. The thermal treatment at 100 and 150°C impaired strongly the strength of the joints, causing an orientation in the 1.2–3.0 kJ/m^2 range.

Although no structural confirmation had been brought forward so far, the above-noted desirable properties of the modified adhesives, as indicated by Millet,[17] might be attributed to copolymerization of ECA and the CPDA ester. In our opinion, however, the homopolymerization rates of ECA and dienoate monomers should be quite divergent so that a substantial degree of copolymerization is not to be expected. It is more likely that the improvement of the adhesive properties at room temperature is at-

tributable to the formation of a two-phase polymer system. Having in mind the composition of the initial monomer mixture, we presumed that this system should contain "soft," rubber-like dispersed phase originating from the CPDA ester and continuous rigid phase originating from ECA. In support of this are both the expanded T_g transition intervals (see Table II) of all CPDA-modified poly(ECA) layers and the superior impact strength performance (room temperature) of all the modified adhesives, comprising up to 20 wt % of the dienoate monomer. Of course, these data must be interpreted with caution until reliable morphological or other proofs are found out.

CONCLUSIONS

The heat resistance of both pure unsaturated 2-cyanoacrylic acid esters and CPDA containing ECA-based adhesive compositions are closely associated with the ability to form crosslinks as the polymer film therefrom (or the corresponding bonded joints) are exposed to increased temperatures. The unsaturated CPDA esters are found to be more suitable as heat resistance promoters than the saturated ones.

Although similar σ_s^{100} and σ_s^{150} values are registered for ACA- and ACPD-modified ECA adhesive, in the latter case the crosslink formation is found to run at temperatures, not causing any depropagation of the polymer structure. Another advantage of the adhesive mixtures is their superior σ_s^{init} values

and impact strength properties, especially when certain saturated CPDA esters are used.

The chemical composition of the polymer films has an important influence upon their adhesive performance. In that connection, the use of ECA-based adhesive compositions improves the versatility of the pure cyanoacrylates because by varying the type and concentration of dienoate modifier employed a softer or more rigid polymer structure could be obtained, whereas the properties of the pure cyanoacrylate monomers are limited by their definite chemical structure.

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