

Electron-beam curable structural adhesives. Part 1: Study of acrylic resins for structural adhesive applications

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(Received 19 April 1994; revised 1 June 1994)*

Different commercial acrylic resins, which can be cured via electron-beam radiation, have been selected for structural adhesive applications. This paper presents and discusses their most important bulk characteristics after radiation curing and their evaluation as adhesives by measurement of the single lap shear strength on stainless steel. The relationships between structure and adhesion on the one hand, and between mechanical properties and adhesion on the other, are discussed.

(Keywords: acrylic prepolymers; electron-beam curing; structure/property relationships)

INTRODUCTION

Structural adhesives are generally thermosetting. The most important families are epoxy, acrylic, polyurethane and phenolic adhesives. Some commercial adhesives are photocured with ultraviolet light, but their uses for structural applications are limited. As regards electron-beam curing, no commercial structural adhesive exists, and very few investigations have been carried out to date.

Yet radiation curing offers many advantages over thermal curing. Probably the most important is the capability to effect very fast cures at ambient temperature, hence leading to a reduction of work time and energy consumption.

Two large families of structural adhesives can be suitable for this process of cure: acrylics, polymerizable by a radical process, and epoxies, polymerizable by a cationic process.

The behaviour of acrylic resins under an electron beam and their thermal and mechanical characteristics after curing are better known than those of epoxy resins. Thus, we mainly studied electron-beam curable acrylic structural adhesives. This investigation included two parts:

- 1) the study of acrylic resins and the relationships between their structure and their properties (thermal, mechanical and adhesive), after radiation curing; and

- 2) the development of adhesive formulations and their characteristics.

The first topic is the subject of this paper.

PREVIOUS DEVELOPMENTS

The first acrylic adhesives, which were brittle, were two-part systems mainly composed of (meth)acrylic monomers and a redox system capable of generating free radicals. This therefore gave the first idea of incorporating a high molecular weight acrylic-modified urethane prepolymer to improve the flexibility and therefore the peel, cleavage and impact resistance. However, it resulted in a reduction of shear strength and heat resistance.

In the 1970s appeared the toughened acrylic adhesives, also generally called second-generation acrylics, reactive adhesives or modified adhesives. They are two-part, room temperature curing adhesives, whose compositions, as suggested in several patents¹⁻²⁰, indicate the same concept: an elastomer is dissolved or colloiddally dispersed in a mixture of addition polymerizable monomers or in a monomer/oligomer/polymer solution. The system is then polymerized using free radical generators, an initiator in one part and an activator in the other. As the polymerization of these monomers proceeds, the elastomer is precipitated in the form of small particles while some graft polymerization of the elastomer with the monomers occurs. These

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elastomeric domains can absorb fracture energy and prevent crack propagation; so a higher resistance to peel, cleavage and impact forces is obtained.

For improved heat resistance, epoxy-acrylate oligomers such as acrylic-modified bisphenol-A epoxies have been used as the basis of structural acrylic adhesives¹⁸.

As regards electron-beam curable structural acrylic adhesives, the only investigations have been carried out by Campbell and co-workers^{21,22}. They first tested mixtures of an acrylic-modified bisphenol-A epoxy prepolymer with three different reactive diluents to bond aluminium alloy lap shear specimens. These were cured by exposure to electron-beam radiation (100 kGy) at room temperature under contact pressure only and provided shear strengths of the order of 11–12 MPa. These values were found to be superior to those of thermally cured assemblies which were bonded together with the same formulations, catalysed with organic peroxides and cured with heat and pressure.

Commercially available modified thermosetting acrylic adhesives were also used to bond aluminium alloy lap shear specimens under the same conditions of cure. The shear strengths obtained were of the order of those provided by the same adhesives after thermal curing (< 15 MPa).

The behaviour of acrylic resins under electron-beam radiation is more well known than that of methacrylate monomers alone. So, we decided to use an acrylic or a

methacrylic resin as the basis of structural acrylic electron-beam curable adhesives.

SELECTION OF ACRYLIC RESINS

Various commercial acrylic resins, exhibiting a good behaviour under electron-beam radiation and good thermal and mechanical strengths after radiation curing, have been chosen.

We present results obtained with five of them. They have various chemical structures that have been identified or verified by ¹H n.m.r. spectroscopy at 250 MHz. The resins are acrylic- or methacrylic-modified epoxy and acrylic-modified urethane prepolymers. Their chemical structures are described in Table 1:

- resin 1 is a short aliphatic acrylic-modified urethane (SNPE);
- resin 2 is an acrylic-modified polyether/aromatic urethane (SNPE);
- resin 3 is a dimethacrylate of diethoxylated bisphenol-A (Akzo);
- resin 4 is an acrylic-modified bisphenol-A epoxy (DGEBA-type) prepolymer (SNPE); and
- resin 5 is an acrylic-modified bisphenol-A epoxy prepolymer (DGEBA-type) with two succinate groups (UCB).

These resins present some interesting differences as

Table 1 Chemical structures of commercial acrylic resins

Resin	Chemical structure
1	$\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}-\underset{\text{H}}{\text{CH}_2}\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\underset{\text{CH}_3}{\text{C}}-\text{CH}_2-\underset{\text{H}}{\text{N}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\text{CH}_2$
2	$\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}-\underset{\text{H}}{\text{C}_6\text{H}_4}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\left(\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{O}\right)_n-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}-\underset{\text{H}}{\text{C}_6\text{H}_4}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\text{CH}_2$
3	$\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-\overset{\text{CH}_3}{\text{C}}-\text{C}_6\text{H}_4-\text{O}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{CH}_3}{\text{C}}=\text{CH}_2$
4	$\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\left(\text{O}-\text{C}_6\text{H}_4-\overset{\text{CH}_3}{\text{C}}-\text{C}_6\text{H}_4-\text{O}-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_2\right)_n-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\text{CH}_2$
5	$\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\underset{\text{CH}_3}{\text{CH}_2}\text{CHO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\left(\text{CH}_2\underset{\text{OH}}{\text{CH}}\text{CH}_2\text{O}-\text{C}_6\text{H}_4-\overset{\text{CH}_3}{\text{C}}-\text{C}_6\text{H}_4-\text{O}\right)_n-\text{CH}_2\underset{\text{OH}}{\text{CH}}\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\underset{\text{CH}_3}{\text{CH}_2}\text{CO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\text{CH}_2$

regards their structure as well as their physical aspect. Indeed, they can be liquid (methacrylic-modified epoxy without hydroxyl groups) or almost solid at room temperature (acrylic-modified aromatic urethane). This is proved by their viscosities, which were measured with a CARRI-MED rheometer and are listed in Table 2.

EXPERIMENTAL PROCEDURES

Radiation curing

Irradiation of samples was carried out at Aérospatiale Aquitaine with a 10 MeV electron-beam accelerator, which can develop 20 kW of power. All samples were electron-beam cured in the same cinematic conditions and with a constant dose rate. The exposure time of each specimen to the radiation was of the order of seconds.

Determination of optimum radiation dose and glass transition temperature

To determine the optimum dose, the resins were cured with electron-beam irradiation over a wide range of doses, after which the glass transition temperature (T_g) was measured for each dose by dynamical mechanical analysis (Du Pont DMA 982 instrument), at a heating rate of 5°C min^{-1} .

The values of T_g reached a maximum, corresponding to a maximum conversion of the double bonds. This value was adopted as the optimum dose and used for further testing.

Extent of cure of the double bonds

This was quantitatively measured for the first three polymerized resins by infra-red (i.r.) spectroscopy. This method consists of comparing, before and after curing, the intensities of bands at 1635 or at 810 cm^{-1} , corresponding to the vibrations of the double bonds.

For the two other resins, the degree of cure of the double bonds was only evaluated by comparison of the Fourier transform i.r. spectra before and after curing.

Bulk mechanical properties

Mechanical properties of cured resins were evaluated with an Instron 1195 mechanical testing machine. Tensile strength (σ_R), Young's modulus (E) and maximum elongation ($\Delta l/l$) were determined using ISO 1 tensile specimens, tested at a constant crosshead speed of 5 mm min^{-1} .

Adhesive properties

The above resins were evaluated alone as adhesives by measurement of the single lap shear strength on stainless steel (quality: ZIO CNT 18 or 304L).

Preparation of adhesion test specimens. Prior to bonding, the stainless steel strips were sand-blasted with $500\text{ }\mu\text{m}$ Corindon, degreased with methyl ethyl ketone and dried. The length and width of the adhesive joints were as recommended in NFT 76-107, with or without calibrating their thickness (calibration: 0.2 mm). The resins were applied to one of the surfaces to be joined as a thin film; the two substrates were then brought together and tightly wrapped to maintain their configuration during handling and cure. It should be noted that resin 2 was heated to approximately 40°C to ensure adequate wetting of the surfaces.

Characterization of adhesive joints. Irradiations were conducted, with the corresponding optimum dose, in air and at room temperature. The lap shear strengths of the radiation-cured resins were also tested at room temperature, following NFT 76-107, using an Instron 1195 dynamometer, at a crosshead speed of 0.5 mm min^{-1} .

RESULTS AND DISCUSSION

Table 2 reports the viscosity, optimum radiation dose, thermal and mechanical characteristics after curing of these acrylic resins. The five selected commercial acrylic resins exhibit characteristics corresponding to the criteria required for this study.

Table 2 Characteristics of the acrylic resins

Resin	Viscosity (Pa s)	Optimum dose ^a (kGy)	T_g ($^\circ\text{C}$)	Tensile properties		
				τ (MPa)	E (MPa)	$\Delta l/l$ (%)
1	16.4/20 $^\circ\text{C}$	20/10	110	83	2900	5.5-7
2	310/40 $^\circ\text{C}$ 31/60 $^\circ\text{C}$	50/10	70	55-62 ^b	3100	16
3	1/20 $^\circ\text{C}$	100/25	100	40	3000	2
4	3880/20 $^\circ\text{C}$	100/25	160	65	3650	2-3
5	2910/20 $^\circ\text{C}$ 6.5/60 $^\circ\text{C}$	50/10	85	58-65 ^b	3100	7-10

^a/ means 'per pass of

^b Values at break and at the maximum (viscoelastic behaviour)

^c The average of five measurements or the worst and the best values

Curing

The optimum radiation doses are not greater than 100 kGy, and resin 1 needs only a 20 kGy dose to cure; these doses can be considered as weak.

The degree of cure of the double bonds, determined quantitatively, is about 98% for the two radiation-cured acrylic-modified urethanes (resins 1 and 2) and about 95% for the cured methacrylate of diethoxylated bisphenol-A (resin 3). We can evaluate approximately that the acrylic-modified epoxy resins 4 and 5 provide a similar extent of cure to that of resin 3.

Bulk properties

Glass transition temperature (T_g). The values of T_g vary from 70 to 160°C; the best value is obtained with the classical acrylic-modified DGEBA resin 4.

The results first show the effect of the particularly polar functions such as hydroxyl groups: resin 3, which does not contain hydroxyl groups, provides a lower T_g than resin 4, whereas they have about the same chain length (decrease of 60°C).

The results also show the importance of the degree of crosslinking. Indeed, a reduction of the T_g can be noticed when the molecular weight between the crosslinks increases. This is illustrated by the comparison of resins 1 and 2, on the one hand, and resins 4 and 5, on the other:

- the presence of succinate groups in the backbone of resin 5 considerably reduces the T_g (decrease of 75°C compared with resin 4);
- although resin 1 is aliphatic, it exhibits a higher T_g than crosslinked resin 2. However, its molecular weight is half that of resin 2 (500 g mol⁻¹ instead of 1000 g mol⁻¹). Thus, it has twice the urethane groups for a given weight than resin 2. Moreover, polyether chains are well known to give low T_g materials.

Mechanical properties. The selected crosslinked resins provide good tensile properties. We can notice some differences which can permit further correlations between adhesion and mechanical characteristics:

- the Young's moduli are in the order of 3000 MPa, except for the cured classical acrylic-modified DGEBA (resin 4) which gives a relatively superior modulus;
- the tensile strains (τ) span a high range (40 to 83 MPa). It can be noticed that both resins 2 and 5, after curing, exhibit viscoelastic behaviour, with the same moduli and tensile strains; and
- finally, as expected, the maximum elongations of these crosslinked resins are low, but with significant differences the two acrylic-modified urethanes and the highest molecular weight acrylic-modified epoxy produce a higher elongation (> 5%). These results prove the effect of the degree of crosslinking on flexibility and also the importance of the chemical nature of the resin. Indeed, resin 1 is the shortest

selected resin but it produces, after curing, a higher elongation than resins 3 and 4.

Adhesive joint properties

The single lap shear strengths are listed in Table 3. All test data reported represent the average of at least four measurements.

The cured resins provided lap shear strengths with bonded stainless steel specimens of between 7.8 and 12.0 MPa without calibration, and between 6.5 and 9.7 MPa with a 0.2 mm thickness. All failures were found to be adhesive. The best value, obtained with resin 5, corresponds to those obtained by Campbell and co-workers^{21,22} using an acrylic-modified DGEBA resin to bond etched aluminium alloy specimens.

Influence of calibration. As expected, the results show, for every resin, a significant reduction in the value of single lap shear strength when the thickness is calibrated at 0.2 mm. This is in agreement with the bibliographic data, which indicate that the shear strength generally decreases when the bond thickness rises (from a certain value of bond thickness). This increase rises from 7% (resin 1) to 24% (resin 5) and does not depend on the viscosity of the resin as could be expected.

Correlations between shear strength and mechanical behaviour. It can be noticed that the three resins which display the best single lap shear strengths exhibit a higher elongation, but there is no proportionality between these parameters.

This condition of minimum flexibility is certainly necessary for a higher strength but is not unique. For example, the acrylic-modified urethane resin 2 provides a lap shear strength similar to that of resin 1 although it is much more flexible. Similarly, resin 5 is less flexible than resin 2 and it also provides the best single lap shear strength.

On the other hand, no correlations between adhesion and E or τ can be found.

Correlations between adhesion and chemical structure. Both of the acrylic-modified urethane resins give similar and relatively high single lap shear strengths. This shows the importance of the high polarity provided by the urethane groups.

Table 3 Single lap shear strengths of acrylic resins

Resin	σ_R (MPa)	
	With thickness calibration $e = 0.2$ mm	Without thickness calibration
1	8.2 ± 0.9	0.8 ± 1.1
2	8.7 ± 0.9	10.1 ± 0.9
3	6.5 ± 0.5	7.8 ± 1.0
4	7.0 ± 0.2	
5	9.7 ± 0.7	12.0 ± 1.0

Yet their polarities are different: as previously mentioned, resin 1 presents twice the urethane groups of resin 2. On the other hand, resin 1 is more rigid, which can explain why it does not give a better adhesion.

As expected, the lowest single lap shear strength is obtained with the dimethacrylated diethoxylated bisphenol-A which does not contain very polar hydroxyl groups and produces a low elongation.

With about the same elongation, in spite of the presence of hydroxyl groups, the acrylic-modified epoxy resin 4 gives only a slightly higher strength than resin 3. Moreover, this strength is significantly inferior to those given by the acrylic-modified urethane resins. Without doubt, it is due to its far lower flexibility.

Likewise, resin 5, which is also an acrylic-modified DGEDA-type resin but which contains two succinate groups, produces the best lap shear strengths. The succinate groups do not generate a very high polarity. So, this good value is certainly due to its flexibility.

CONCLUSION

The selected commercial acrylic resins can be radiation-cured at a moderate dose (<100 kGy) to achieve very satisfactory lap shear strengths with bonded stainless steel specimens (especially with three of them) reaching 8 to 12 MPa.

It is not easy to make correlations between chemical structure and adhesion on the one hand, and between rheological behaviour and adhesion on the other hand, because both of them must have a great influence:

- very polar functions, such as urethane or hydroxyl groups, are particularly important because of the possibility to create hydrogen bonds with the oxides and hydroxides present on the metal surface;
- on the other hand, some flexibility seems to be necessary to obtain a good lap shear strength.

These first results constitute an encouraging and informative basis to make further investigations on the formulation of electron-beam structural adhesives. This topic will constitute the second part of our investigations.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Aérospatiale for its financial support and contribution to this investigation.

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