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Thermochimica Acta 396 (2003) 199–210

thermochimica acta

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Electron-beam curing of a novel liquid crystal thermoset resin

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Received 31 December 2001; received in revised form 4 October 2002; accepted 7 October 2002

Abstract

In this paper we report on the processing and properties of a novel, “dual-curing” liquid crystal (LC) resin cured by electron-beam irradiation. The LC monomer contains both acrylate and acetylene reactive groups. Neat resin samples were e-beam cured in either the LC phase at 65 °C or the isotropic phase at 90 °C. The experimental variables included the total e-beam radiation dose (150 or 250 kiloGray {kGy or J/g}) and thermal post-cure cycle (none or 190 °C/1 h). Cured polymer specimens were characterized by dynamic mechanical analysis (DMA) and thermo-mechanical analysis (TMA). The results demonstrated that e-beam exposure alone at 150 or 250 kGy was not sufficient to fully cure the polymer, although it was sufficient to lock-in the isotropic or LC morphology. Differences in morphology had a significant impact on the DMA and TMA results for non-post-cured specimens, where LC samples demonstrated more robust mechanical properties at elevated temperatures compared to isotropic specimens. After a thermal post-cure cycle the DMA storage modulus differences between the LC and isotropic samples were not as great. However, large differences in thermal expansion coefficients remained. The data suggest the possibility that the acrylate bonds react during e-beam exposure, followed by conversion of the acetylene bonds during the thermal post-cure. Also, e-beam curing in the LC phase likely will allow for tighter molecular packing and more efficient polymerization resulting in higher crosslink densities.

Keywords: Liquid crystalline polymers; Reactive liquid crystals; Electron-beam curing; Thermal analysis

1. Introduction

Crosslinked network polymers are widely used in structural applications such as advanced composites and adhesives. In recent years, several new approaches have been applied to advance the capabilities of these materials. One such approach is the formation of network polymers from liquid crystalline (LC) monomers that self-assemble into meso-phase (intermediate between crystalline and liquid) LC domains within a specific temperature range, followed by thermal or photocuring in that temperature range to lock-in the LC morphology [1–6]. Highly crosslinked networks also have been formed from monomers that undergo a phase change into a liquid crystalline state *during* the polymerization reaction [7–9]. Because of their rigid rod structures, these materials possess the desirable properties of high stiffness and high thermal stability (e.g. $T_g > 300\,°C$) whether polymerized in the LC or isotropic phase. However, the LC morphology acts as a crack deflector and improves toughness in cured specimens, compared to the same compound cured in the isotropic phase [10]. In addition, LC molecules

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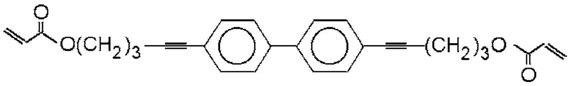
PII: S0040-6031(02)00519-1

can be oriented with shear or magnetic fields to produce networks with anisotropic mechanical and physical properties [5,6].

Another approach to forming structural networks is from acetylene-terminated resins [11,12]. These acetylene-based resins have advantages over epoxy resins because of the moisture resistance of the reactants and the crosslinked polymer as well as the improved thermal stability of the networks formed. Previous research [10,13] conducted at the University of Dayton has focused on synthesis and network formation of “dual” functional monomers. One of these that is both liquid crystalline and has two reactive acetylene groups is shown below.



Monomer 1

In addition to the acetylene groups, the monomer contains terminal acrylate groups. The presence of both reactive moieties gives it the “dual” curing capability. Crosslinking of the monomers can proceed first through low temperature thermal or e-beam curing of the acrylate groups, followed by higher temperature curing of the acetylene groups. This dual-curing capability allows increased flexibility in the processing of the materials for various applications. Monomer **1** exhibits a liquid crystal phase between 50 and 70 °C (smectic phase). This phase is characterized by dense packing of the rigid rod monomers in planes. If curing is conducted while the monomer is in the liquid crystalline state, the resulting crosslinked structure is expected to possess several favorable characteristics, such as a high glass transition temperature and as other good high temperature properties, high toughness, and reduced shrinkage.

2. Objectives

The processing, behavior, and properties of the polymer formed from monomer **1** during e-beam irradiation are the focus of the current study. Network formation from monomer **1** also can occur thermally via free-radical addition polymerization of the acrylate groups, the acetylene groups, or both. For neat monomer **1** the thermal reactions proceed spontaneously at a temperature of approximately 190–240 °C. With the addition of thermal initiators such as benzoyl peroxide, a sufficient degree of polymerization can be achieved at a low temperature (e.g. 65 °C) such that the liquid crystal morphology is locked in before proceeding to a higher temperature post-cure [14]. However, the addition of thermal initiators reduces the shelf life of the monomer and limits processability. In the current study, *no thermal initiators were used*. The goal was to demonstrate that low-to-moderate temperature e-beam curing is sufficient to lock-in the LC morphology. A subsequent thermal post-cure cycle was used to complete the cure and improve the properties of the initially e-beam crosslinked material.

A longer-term goal is to demonstrate that liquid crystal thermosets, such as those based on variations of monomer **1**, offer outstanding properties such as toughness, high temperature and environmental durability, low coefficient of thermal expansion (CTE), and ease of processing. Furthermore, it is possible that many of these properties may be tailored through alignment of the LC domains with shear or magnetic fields. The current study represents the first to examine the use of e-beam irradiation with a dual-curing LC monomer.

3. Experimental

Experimental procedures were developed to expose heated, neat resin samples of monomer **1** to electron-beam irradiation. Rectangular molds with a 55 mm × 15 mm × 1 mm open-top cavity were fabricated using silicone rubber. A thin (0.07 mm diameter wire) type K thermocouple was placed in one end of the mold via a slit made through the mold wall. Molds were treated with a release spray and placed on a thin (1.57 mm) aluminum plate in a heated oven at 100 °C. Approximately 1 g of pure monomer **1** powder was sifted into the mold and allowed to melt. After the mold was full, the oven was evacuated in order to degas the liquid resin for 20 min. After returning to atmospheric pressure, a 1 mm thick glass microscope slide (which was also placed in the oven before degassing) was slid over the top of the mold from one side to the other, with care being taken to avoid trapping air bubbles. The purpose of the glass slide was

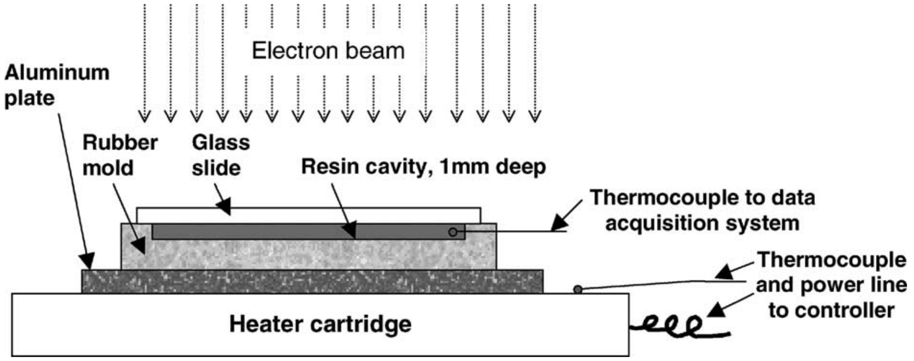


Fig. 1. Experimental apparatus for exposing heated, net resin samples to e-beam irradiation.

to prevent oxygen inhibition during e-beam cure and to reduce thermal gradients through the thickness of the resin. Differential scanning calorimetry (DSC) was used to establish that no significant cure reaction occurred during the degassing process.

After degassing, the mold assembly was placed in the e-beam vault and onto a heater cartridge (see Fig. 1). The heater was controlled via a surface-mounted thermocouple and temperature controller placed outside the vault. The thermocouple in the mold was connected to a relay panel and monitored with a computer data acquisition system located outside the vault.

Monomer **1** was e-beam cured in the isotropic phase at 90 °C and LC phase at 65 °C. No attempt was made to align the LC domains in this study. The e-beam was generated with a pulsed linac (linear accelerator) operated by the University of Dayton. The following parameters were used in the current study: beam energy 3 MeV, beam current 100 mA per pulse, pulse width 5 μs, pulse rate 50 Hz, and scan width 15 cm. Samples were translated under the beam at a speed of 35 cm/min. A total dose of either 150 or 250 kGy (J/g) was deposited in increments of 5 kGy per pass. Each pass required approximately 30 s to complete. The process was typically stopped after every eight passes to avoid excessive temperature rises due to heat of reaction and radiative heat input to the mold assembly.

After e-beam curing, samples were cooled and demolded. It was necessary to destructively remove the rubber mold from each sample. From each resin plaque, several samples for thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA) were obtained by cutting with a fine-toothed saw blade. TMA conditions were as follows: macroexpansion mode, 5 °C/min heating rate, argon atmosphere, 0.2 g static weight, 0.05 N force. These conditions were selected to allow for appropriate probe contact with the specimen and for free expansion and relaxation of residual frozen cure stresses. DMA conditions were as follows: TA Instruments 2980 DMA, thin-film tensile mode (specimens ∼1 mm thick, ≥25 mm long), 2 °C/min heating rate, 3 μm strain amplitude, 0.01 N static force, 1 Hz oscillation frequency, air atmosphere. Some of the specimens were post-cured in air at 190 °C for 1 h. The curing in air duplicates the processing conditions normally followed for these materials in industry. These polymers are thermostable and did not exhibit any noticable oxidation during the post-cure cycle (as confirmed by FTIR analyses; see further comments in Section 4.3.1). This was a preliminary study with a 2^3 full factorial experimental matrix. The conditions that were considered are summarized in Table 1.

Loctite 334 an acrylate structural adhesive (without activator) was used as a reference material. It

Table 1
Material and process factors examined in this study

Factor	Level	
	−	+
Monomer **1** morphology (temperature during e-beam cure)	Isotropic (90°)	Non-aligned LC (65 °C)
E-beam dose	150 kGy	250 kGy
Thermal post-cure	None	190 °C for 1 h

was degassed at 50 °C, e-beam cured at 40 °C, and did not receive a thermal post-cure. This and other acrylate-based adhesives by Loctite have been used in previous studies involving e-beam resin and adhesive development [15,16]. Loctite 334 was the most widely used commercially available e-beam curable adhesive as of 1996 [16]. Although many new e-beam curable resins have been developed since then [17], they are generally based on cationic epoxy formulations. Thus, Loctite 334 was chosen for this study since, similar to monomer **1**, it is based on acrylate chemistry.

4. Results and discussion

4.1. Sample preparation

DSC data for neat monomer **1** before and after degassing are shown in Fig. 2. The purpose of the degassing was to remove air entrained in the sample arising due to melting of the original powder. There was no weight loss due to removal of volatiles on degassing. The two DSC endotherms correspond to the crystalline-to-LC transition (∼50 °C) and LC-to-isotropic transition (∼70 °C). The broad exotherm centered at 240 °C is caused by the thermal reaction of the acrylate and acetylene groups. The effect of the degassing process on monomer **1** is minor: a majority of the primary exotherm remains intact, the endothermic transitions also are relatively unaffected, and the heated resin was observed to be in a state of low viscosity (i.e. 10–100 cp) after degassing (slight differences in the DSC curves can be attributed to some differences in the mass of sample used in each case; there is a slight endotherm in the degassed sample at around 150 °C origin unknown currently). Based on this it was concluded that no significant polymerization occurred as a result of vacuum degassing at 100 °C for 20 min.

This result demonstrates an advantage of e-beam curing-improved shelf life and processability of resins. Because a thermal initiator is not required, one has more flexibility in processing using moderate or high temperatures to obtain excellent neat resin or prepreg specimens. This result also demonstrates a desirable characteristic of LC monomer **1**: the existence of a low viscosity isotropic phase. Thus, if necessary, we can switch between the low viscosity (isotropic phase) or high viscosity (LC phase) during processing by making a slight adjustment in temperature.

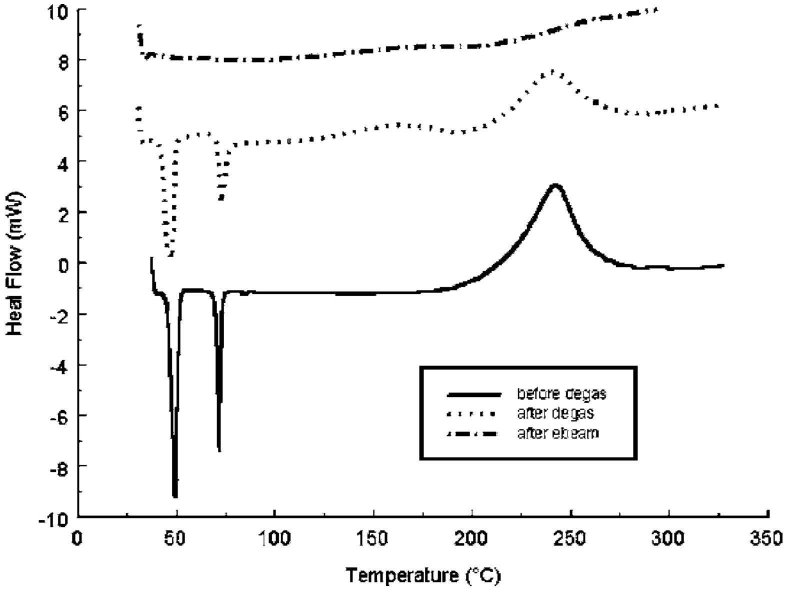


Fig. 2. DSC results for neat monomer **1** before and after 20 min vacuum degas at 100 °C, and after e-beam exposure of 150 kGy. DSC heating rate was 5 °C/min, sample size ∼3 mg.

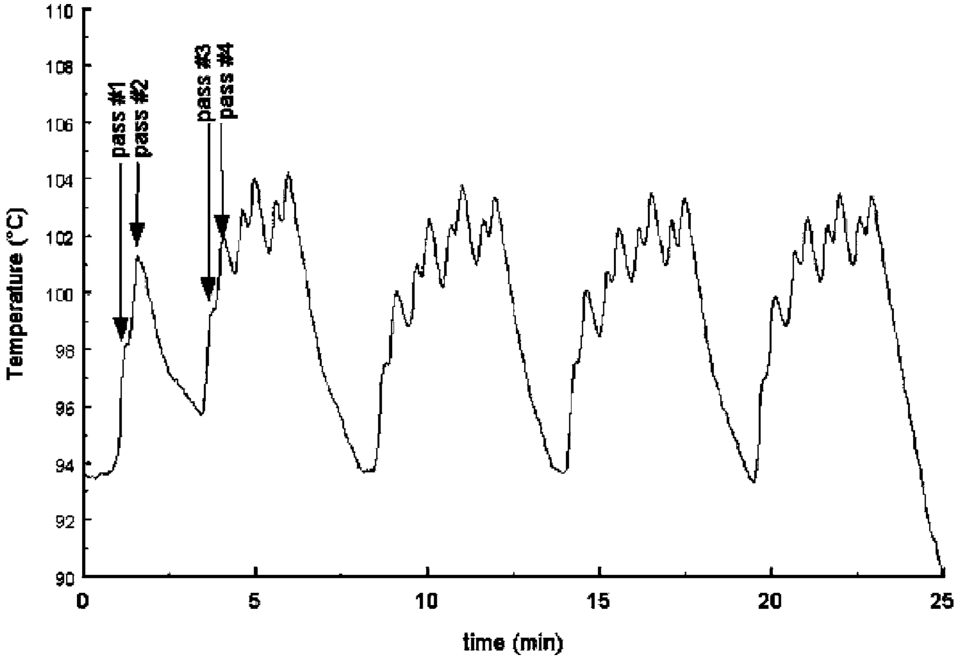


Fig. 3. Real time, in situ temperature profile of monomer **1** during e-beam cure. The sample was exposed to a cycle of two initial passes, a cycle of six passes, and 3 cycles of eight passes each. The beam was off during the cool down period of 2–3 min in between cycles. Note sample thermocouple position in Fig. 1.

4.2. Sample curing

The temperature profile observed for the resin during e-beam cure is given in Fig. 3. Two mechanisms contribute to the overall temperature rise: exothermic heat of reaction and radiation energy absorption. The exothermic heat of reaction, although currently unknown as a function of e-beam dosage, was expected to affect the temperature rise minimally in this study due to the small sample size, large surface area of contact with the mold, and low dose per pass. The second mechanism contributing to heat rise is applicable to all materials. A commonly accepted approximation for calculating heat rise due to radiation absorption under adiabatic conditions is given by

$$\Delta T = \frac{\text{dose}}{C_p}$$

where ΔT is the temperature rise (°C), dose is given in unit of kGy (i.e., J/g), and C_p is the specific heat (J/g °C) of the material. Typical values of specific heat for polymeric materials (such as monomer **1** and silicone rubber), glass, and aluminum are 1.2, 0.8, and 0.9 J/g K, respectively. Although the dose varied throughout the thickness of the experimental apparatus, it is important to note that all mold components received some dose. Using the *measured* dose in the resin chamber (5 kGy per pass) as the average dose for the entire mold assembly, a temperature rise of about 5 °C per pass was expected. From Fig. 3, this value was observed only for the first pass of each cure cycle. After the first or second pass of each cycle, the temperature rise reached a steady-state value of about 2 °C.

These results warrant further investigation. Generally, it is imperative to know the precise temperature of the polymer with confidence in order to control the LC phase behavior. Future studies will examine some of the important processing issues in more detail. These include the heater controller dynamics during e-beam exposure, heat transfer to the environment, and the effect of the thermocouple absorption of radiation energy. For example, during e-beam exposure, the thermocouple may be at a different temperature than the surrounding resin. However, this will not explain the observed response because the thermocouple metal heat capacity is about 0.5 J/g °C, and therefore an instantaneous temperature rise on the order of 10 °C per pass would be expected instead of the lower values actually observed.

Regardless of the difficulties involved in obtaining accurate temperature measurements during e-beam cure, the apparatus was sufficiently accurate to ensure that monomer **1** was cured with either isotropic or LC morphology. By visual observation, the cured isotropic and LC samples were transparent and opaque, respectively, as expected. Microscopic analysis for birefringence of the LC samples confirmed the LC morphology. Thus, an e-beam exposure of 150 kGy was sufficient to lock-in the morphology.

4.3. Thermal analysis

DSC results (see Fig. 2) indicated a high degree of conversion upon e-beam exposure (i.e. significant reduction in the cure exotherm). However, previous experience with thermal curing of monomer **1** has shown that DSC results do not necessarily correlate with mechanical strength development [14]. A more reliable measure of mechanical performance is given by TMA and DMA results.

4.3.1. Thermomechanical analysis (TMA)

Three types of information can be obtained from TMA analysis. The linear CTE is the slope of the curve, the glass transition temperature is indicated by an increase in slope upon heating, and additional curing and shrinkage corresponds to the temperature where the slope becomes negative (i.e. sample ceases to expand with rising temperature). The CTE was measured for all samples in the temperature range of −50 to 0 °C (glassy state). All the values were in the range 50–100 μm/m °C, which is consistent with previous results involving purely thermal curing of monomer **1** in isotropic and non-aligned LC phases.

Fig. 4 illustrates the effect of e-beam dose and post-cure on isotropic samples. Curves 1 and 3 display a marked increase in slope at about 50 °C, while curves 2 and 4 change more gradually from low to high slope from −100 to 250 °C. This indicates that the post-cure was responsible for increasing the glass transition. Regarding the temperature for residual cure shrinkage (i.e. when the curves begin to decrease or “roll over”), the electron dose was the controlling

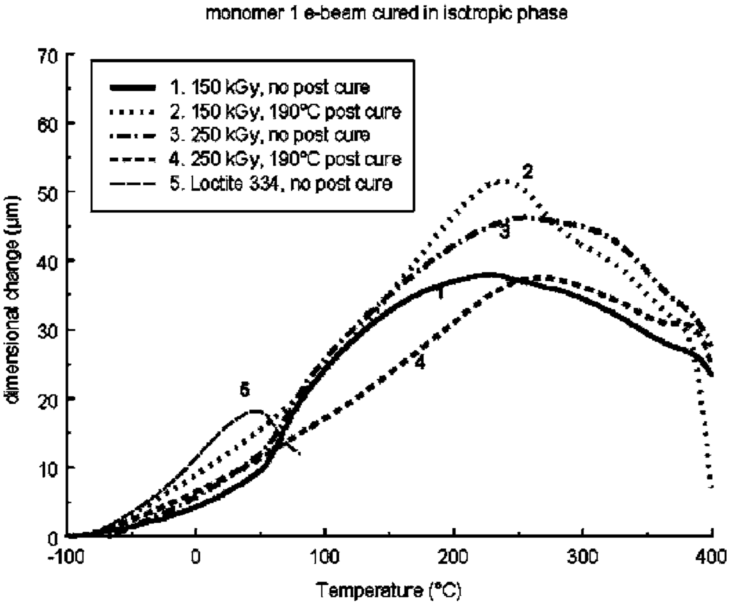


Fig. 4. TMA linear expansion results comparing dose and post-cure effects for monomer **1** cured in the isotropic phase.

factor. Curves 3 and 4 (250 kGy) show a maximum at about 275 °C compared to 225 °C for curves 1 and 2 (150 kGy). Loctite 334 begins residual cure shrinkage at or near its cure temperature (∼50 °C). This is in contrast to the monomer **1** samples, in which temperatures for residual curing, even for non-post-cured samples, were significantly higher than the cure temperature. This result may indicate that some conversion of the acetylene groups in monomer **1** is taking place during the e-beam cure. The downturn noted for the TMA curves is attributed to cure shrinkage based on the fact that only a very small load was placed on the specimens, they are already crosslinked and do not soften appreciably beyond T_g, and there was no evidence of probe penetration on the surface of the specimens after measurement. The additional crosslinking is consistent with the increase in modulus observed above T_g in the DMA data reported below.

Fig. 5 illustrates the effect of dose and post-cure on LC samples. Regarding the post-cure effect, curves 1 and 3 (no post-cure) display a marked change in slope at 110 °C while curves 2 and 4 (190 °C post-cure) do not until 325 °C. The glass transition of the non-post-cured LC samples is about 110 °C, while it was about 50 °C for the non-post-cured isotropic samples (Fig. 4). This is surprising, given that the LC samples were e-beam cured at 65 °C and isotropic samples at 90 °C. A possible explanation for both of these results is that in the LC domains there is tighter molecular packing and more efficient polymerization. In contrast, this result was *not* observed for purely thermal curing or UV curing, in which there was little or no difference in TMA (and DMA) results for LC and isotropic samples [5,6,13,14]. We suspect that the high reaction rate of the e-beam polymerization is responsible for these results. If the rate of reaction is fast enough, the molecular orientation that is characteristic of the LC state will not have an opportunity to relax and dissipate during polymerization. On-going research is being conducted to provide additional insights into this.

The highest glass transitions and degrees of crosslinking were obtained by thermally post-curing the samples. This is consistent with data from a previous study involving purely thermal curing of monomer **1** compounded with a peroxide initiator [14]. In that study, it was hypothesized that the acrylate bonds were cured at low temperatures locking-in the LC or isotropic morphology, and the acetylene bonds were converted at higher temperatures (175–250 °C), producing a high degree of crosslinking. In the current study, a similar result may be hypothesized, involving

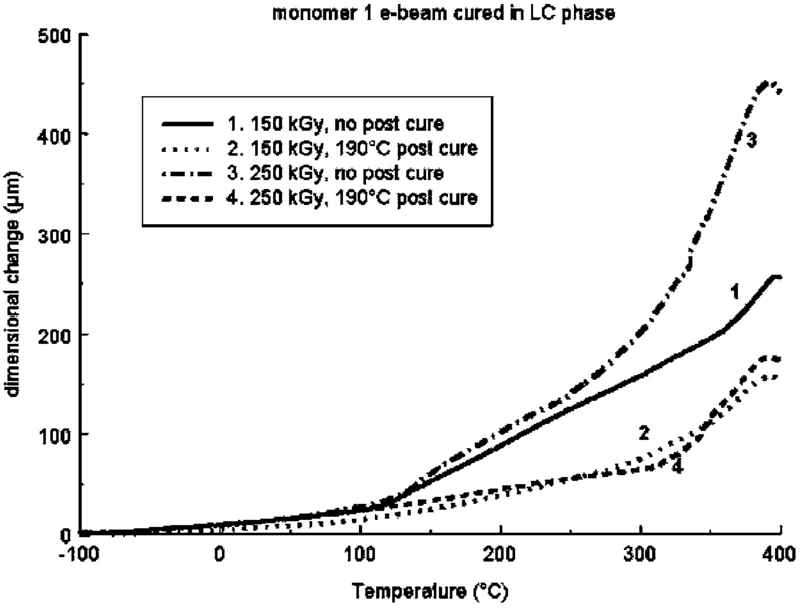


Fig. 5. TMA linear expansion results comparing dose and post-cure effects for monomer **1** cured in the LC phase.

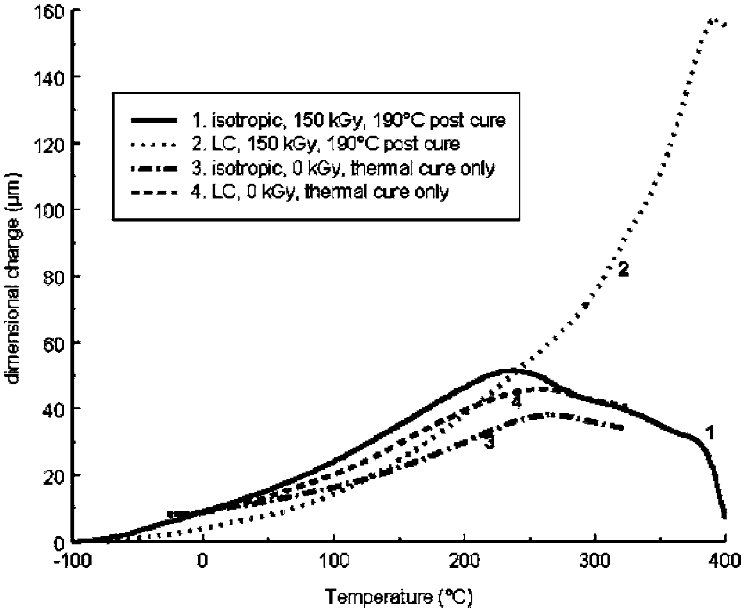


Fig. 6. TMA linear expansion results comparing monomer **1** cured in different ways, all involving a post-cure. Data for lines 3 and 4 were taken from a previous study [14] which involved compounding monomer **1** with benzoyl peroxide and curing up to 175 °C.

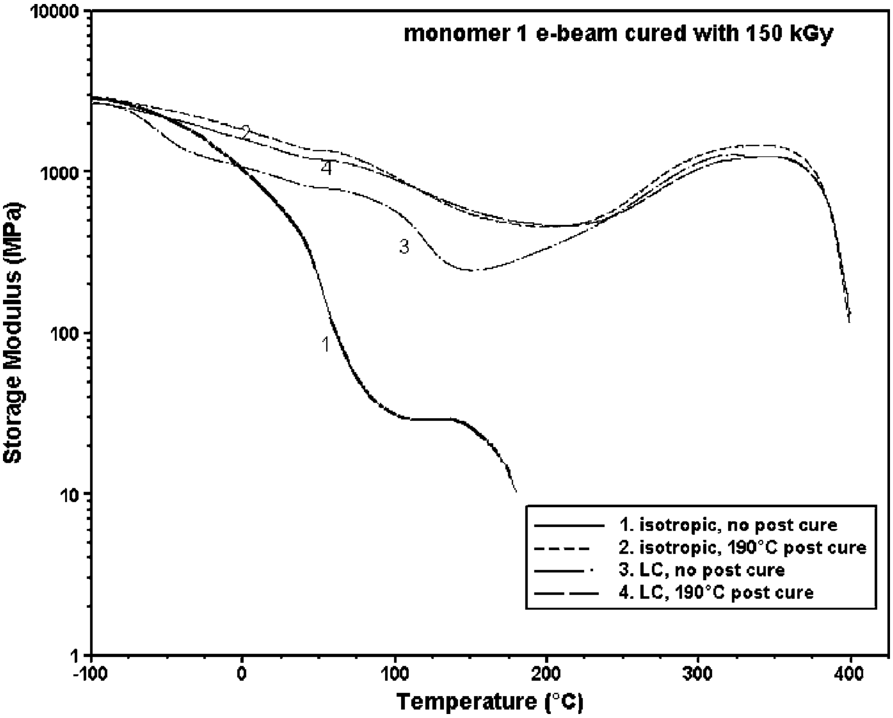


Fig. 7. DMA storage modulus (E') results showing effects of phase morphology and post-cure cycle on monomer **1** e-beam cured with 150 kGy.

curing of the acrylate bonds via e-beam exposure followed by conversion of the residual acetylene bonds during the thermal post-cure. It is possible that a small amount of acetylene conversion also may occur during e-beam cure. This is consistent with results in the literature for e-beam curing of other diacetylene compounds, in which an extremely high dosage (1000 kGy) was required to produce a minor level of acetylene conversion (e.g. 25%) [18]. Work is in progress using infrared and Raman spectroscopy to confirm this result for monomer **1**. Preliminary results from these studies indicate that a significant concentration of double bonds appears during the thermal post-cure. This is consistent with the proposed reaction sequence involving conversion of the acetylene moieties.

Fig. 6 provides a comparison of the e-beam/post-cured samples to each other (LC vs isotropic) as well as to samples cured with purely thermal exposure. Curves 1 and 3 indicate that the combined e-beam/thermal post-cure of isotropic monomer **1** produces a material with CTE similar to that obtained from purely thermal curing of monomer **1** in the LC state(data taken from [14]). Curve 2, however, indicates that e-beam curing in the LC phase produces a *significantly* different response.

4.3.2. Dynamic mechanical analysis (DMA)

DMA is most useful for characterizing the viscoelastic behavior of polymeric materials at various temperatures. In Figs. 7–10, the tensile storage modulus (E'), and loss modulus (E'') curves for various resin samples are given as a function of temperature. A storage modulus of 10^9 Pa or higher is generally associated with the glassy state. With cured monomer **1** samples, at low temperatures the modulus begins in

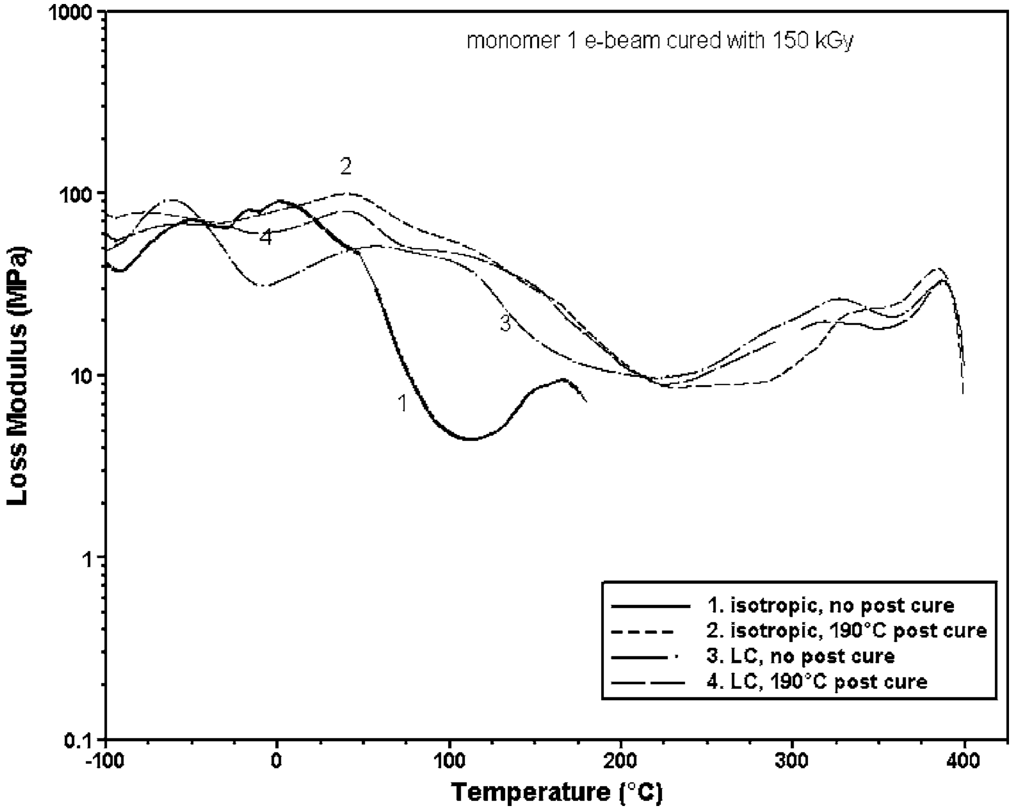


Fig. 8. DMA loss modulus (E'') data corresponding to samples of Fig. 7, reflecting the effects of phase morphology and post-cure cycle on monomer **1** e-beam cured with 150 kGy.

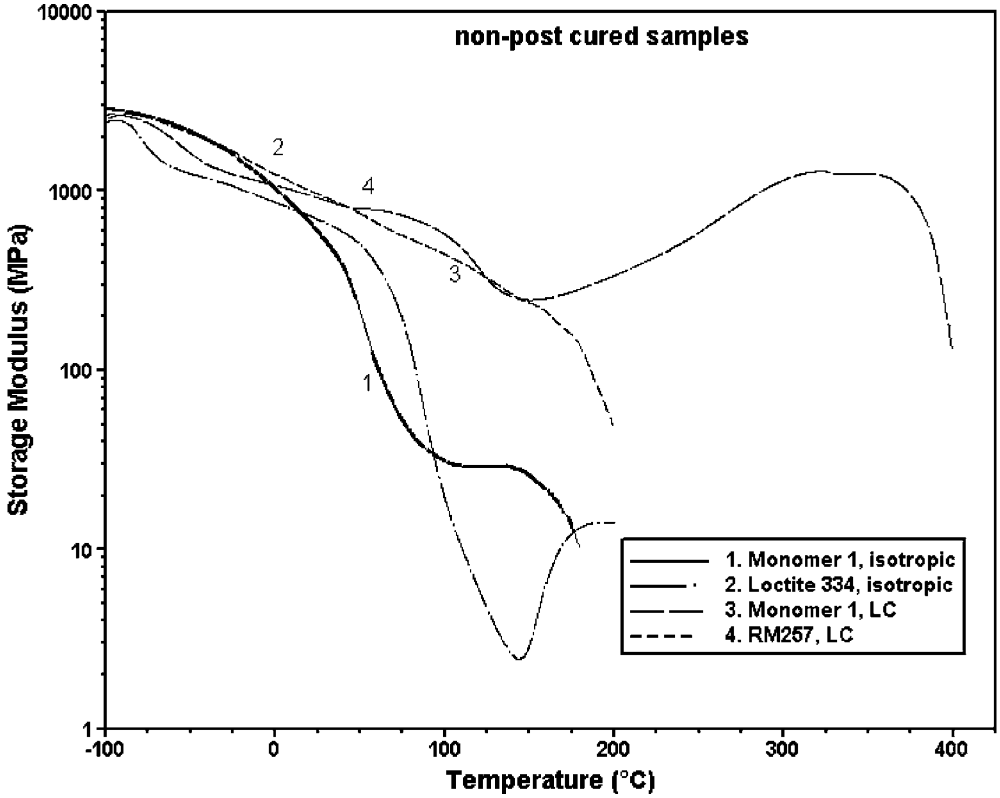


Fig. 9. DMA storage modulus (E') results for various acrylate-based resins e-beam cured with 150 kGy (RM257 was cured with 200 kGy by Science Research Laboratory) with no thermal post-cure.

the glassy state but then goes through a minimum in the temperature range of 100–200 °C. The increase in modulus to the glassy state in the 150–250 °C range is caused by additional crosslinking, most likely due to the acetylene groups as noted earlier. The modulus begins to fall again at $T > 300$ °C after the residual curing has been completed. From previous results involving thermal curing, thermal degradation is the cause of the decrease in E' at 350 °C [14].

Figs. 7 and 8 compare the changes in viscoelastic properties for the LC and isotropic morphologies and post-cure effects for monomer **1** e-beam cured with 150 kGy. As noted previously, the LC state (and morphology) of the sample during e-beam cure makes a significant difference in non-post-cured samples (curves 1 and 3). However, the thermal post-cure cycle causes an increase in E' and reduces the differences in modulus (curves 2 and 4). The effect of the thermal post-cure at 190 °C is significant, producing a crosslinked structure that maintains a high storage modulus up to high temperatures. In each case additional crosslinking is noted at temperatures in excess of 200 °C, with the DMA curves merging above 250 °C. DMA measurements for sample 1 were not carried out to high temperatures due to fracture of the samples during the test. The corresponding loss modulus (E'') data for the samples in Fig. 7 are shown in Fig. 8. The major relaxation seen here is in the glass transition region. However, the non-post-cured LC sample (3) has a noteworthy relaxation at −65 °C which is reduced after post-cure (4).

In Fig. 9 the DMA storage modulus E' data for monomer **1** are compared with those of other reference polymers, where all resins received only an e-beam dose (no post-cure). Monomer **1** in the isotropic phase is compared to Loctite 334, while monomer **1** in the LC phase is compared to RM257. Loctite 334 is consists of a mixture of non-LC aliphatic and aromatic

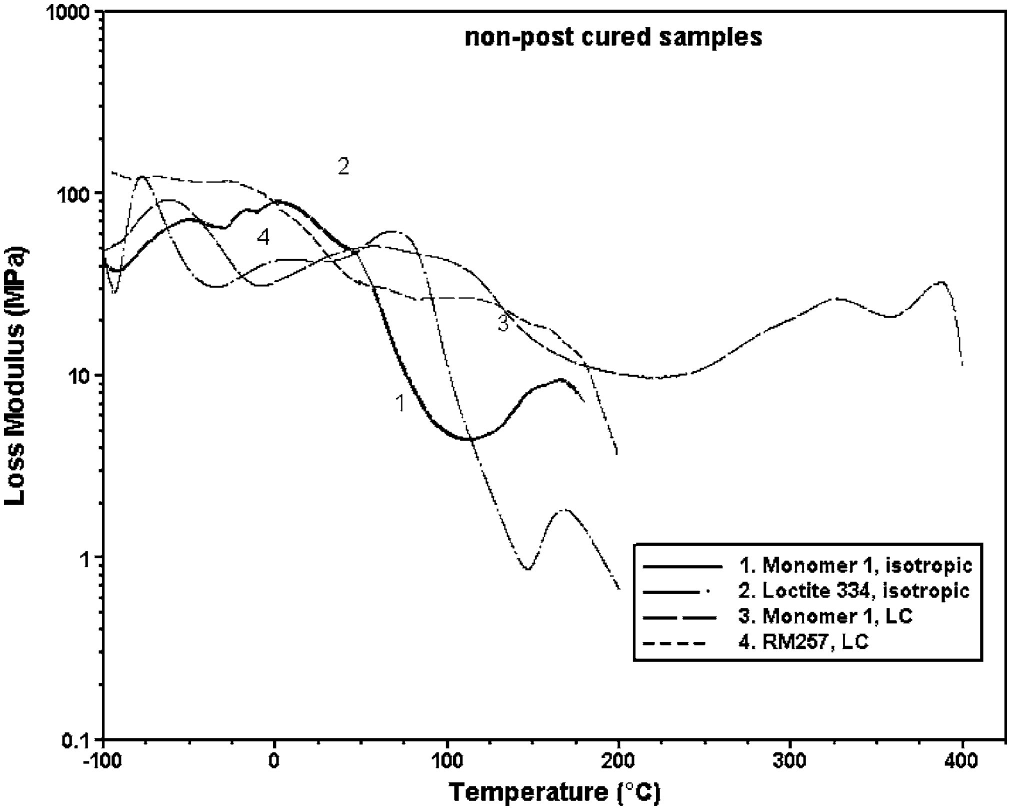


Fig. 10. DMA loss modulus (E'') data for various acrylate-based resins e-beam cured with 150 kGy (RM257 was cured with 200 kGy by Science Research Laboratory) with no thermal post-cure.

main-chain compounds with acrylate side or end groups. RM257 is an acrylate terminated LC resin similar in structure to monomer **1** [5,6], but without acetylene groups. The similarity of the responses (up to 150 °C) based on whether the sample was cured in the isotropic or LC phase is noteworthy. These results are consistent with the TMA results for monomer **1** and the general increase in crosslink density referred to previously, by conducting e-beam curing in the LC phase. As noted previously, additional research is being conducted to provide insights into the nature of the differences in molecular structure between isotropic and LC cured specimens.

The corresponding loss modulus (E'') data for the samples in Fig. 9 are shown in Fig. 10. It is interesting to note that at low temperatures the loss moduli curves for the two LC samples are fairly similar and those for the two isotropic samples have some similarities.

5. Conclusions

- Successful preparation and curing of monomer **1** samples with a combined e-beam/thermal post-cure process was carried out.
- E-beam exposure alone, at dosages commonly used for composite materials (150–250 kGy), was not sufficient to fully cure monomer **1**, although it was sufficient to lock-in the LC or isotropic morphology.
- A post-cure cycle of 190 °C was needed to produce a material that retained a glassy modulus at temperatures up to 350 °C.
- E-beam curing in the LC phase (vs. isotropic) leads to a more highly structured or oriented polymer network, possibly with a higher crosslink density. This is likely due to retention of the close registry of molecules in the LC phase.

- It does not appear that a thermal post-cure cycle eliminates important structural differences between monomer **1** cured by e-beam in the LC phase vs. the isotropic phase. TMA results indicate that significant property differences remain even though the DMA data for post-cured samples compare more closely.

Acknowledgements

The authors are pleased to acknowledge that this work was sponsored by an Air Force Office of Scientific Research Phase II STTR contract # F49620-99-C-0037, "High Performance Liquid Crystal Adhesives". We thank Dr. Charles Lee, the AFOSR contract manager, for his support. E-beam curing was conducted at the University of Dayton's Laboratory for Research on Electron-Beam Curing of Composites. Thanks also go to Dr. Cathy Byrne of Science Research Laboratory, Somerville, MA, for providing financial support to synthesize working quantities of monomer **1**.

References

[1] D.J. Broer, H. Finkelmann, K. Kondo, Makromol. Chem. 189 (1988) 185–194.
[2] H. Andersson, U.W. Gedde, A. Hult, Polymer 33 (19) (1992) 4014–4018.
[3] S. Jahromi, J. Lub, G.N. Mol, Polymer 35 (3) (1994) 622–629.
[4] W. Mormann, Trends Polym. Sci. 13 (8) (1995) 255–261.
[5] J.W. Schultz, R.P. Chartoff, Polymer 39 (2) (1998) 319–325.
[6] J.W. Schultz, R.P. Chartoff, J.S. Ullett, J. Polym. Sci. B 36 (6) (1998) 1081–1089.
[7] M.E. Smith, E.P. Douglas, B.C. Benicewicz, J.D. Earls, R.D. Priester, in: Materials Research Society Symposium Proceedings, vol. 425, 1996, pp. 167–172.
[8] G.G. Barclay, S.G. McNamee, C.K. Ober, K.I. Papathomas, D.W. Wang, J. Poly. Sci. A 30 (1992) 1845–1853.
[9] Q. Lin, A.F. Yee, H.-J. Sue, J.D. Earls, R.E. Hefner Jr., J. Poly. Sci. B 35 (1997) 2363–2378.
[10] J.S. Ullett, T. Benson Tolle, J.W. Schultz, R.P. Chartoff, Thermal expansion and fracture toughness properties of parts made from liquid crystal stereolithography resins, in: Solid Freeform Fabrication Proceedings, University of Texas at Austin, Austin, TX, August, 1998, pp. 519–527.
[11] C.Y.-C. Lee, Developments in Reinforced Plastics, Elsevier, New York, 1986, Chapter 4, pp. 121–150.
[12] H.X. Nguyen, H. Ishida, F.I. Hurwitz, J.P. Gorecki, L. D'Amore, L.H. Hyatt, J. Polym. Sci. B 27 (1989) 1611–1627.
[13] J.W. Schultz, J. Bhatt, R.P. Chartoff, R.T. Pogue, J.S. Ullett, J. Polym. Sci. B 37 (1999) 1183–1190.
[14] A. Popp, Effects of morphology and cross-link density on the properties of a dual-curing, liquid crystalline polymer, M.S. Thesis, University of Dayton, December, 2000.
[15] C.A. Byrne, D. Goodman, G.R. Palmese, J.M. Sands, S.H. McKnight, Electron beam curable adhesives for out-of-autoclave bonding of large composite structures, in: Proceedings of the SAMPE'2000, Long Beach, CA, May 21–25, 2000, pp. 2187–2199.
[16] V.J. Lopata, M. Chung, T.E. McDougall, V.A. Weinberg, Electron-curable adhesives for high performance structures, in: Proceedings of the 39th International SAMPE Symposium, Anaheim, CA, April 11–14, 1994.
[17] C.J. Janke, A cooperative R&D program on interfacial properties of electron beam cured composites, in: 1999 Electron Beam Curing of Composites Workshop Proceedings, Oak Ridge National Laboratory, Oak Ridge, TN, April 20–21, 1999.
[18] P.T. Hammond, M.F. Rubner, Macromolecules 28 (4) (1995) 795–805.