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ACCELERATION OF THE CATIONIC POLYMERIZATION OF AN EPOXY WITH HEXANEDIOL*

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Abstract

Thin films of 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate were UV irradiated (1.1 J cm^{-2}) under isothermal conditions ranging from 0 to 50°C. Under these conditions the polymerization advanced quickly but only to a conversion level of less than 10% before the reaction rate slowed by more than an order of magnitude. This drop off in rate was not caused by the glass transition temperature, T_g, reaching or exceeding the reaction temperature, T_{rxn}, since the epoxide's T_g remained at least 40°C below T_{rxn}. Raising the sample temperature above 60°C caused a sharp increase in the conversion level. At 100°C conversion exceeds 80% and the ultimate T_g approaches 190°C. The addition of 10 mass% 1,6-hexanediol, HD, to the epoxy caused the conversion at room temperature to quintuple over the level obtained without the alcohol present. The heat liberated from this alcohol epoxy blend during cure on a UV conveyor belt system caused the sample's temperature to increase by about 100°C above ambient whereas the epoxy alone under these conditions only experienced a modest temperature rise of about 26°C. If the amount of HD in the blend is increased above 10% the heat of reaction at 23°C decreases due to HD being trapped in a nonreactive crystalline phase. Boosting reaction temperatures above 50°C melts the HD crystals and yields significantly improved conversion ratios. As the level of alcohol blended with the epoxy is raised its ultimate T_g is lowered and when the concentration of alcohol in the blend nears 30 mass% T_g drops below room temperature.

Keywords: acceleration, cationic polymerization, epoxy, glass transition temperature

Introduction

Calorimetry was used to follow the curing reaction of epoxy [1–3]. With an annual market in excess of a billion dollars and a yearly double digit growth rate photoinitiated polymerizations have become one of polymer technologies more exciting and expanding areas of development. Photoinitiated polymerizations, known also as UV curings, have

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* This paper is dedicated to Prof. Karasz to salute him on his 70's birthday

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numerous uses that range from high volume applications like coatings, adhesives and printing inks to lower volume, high technology products such as holographic data storage media, microelectronic encapsulation and photolithography.

Both radical and cationic polymerizations can be initiated by UV light exposure. The latter type of reactions have gained a lot of commercial interest lately with the development of efficient cationic initiators and the fact that, unlike radical processes, cationic reactions are not inhibited by oxygen [4, 5]. Due to their excellent end use properties such as good adhesion to other materials, superior mechanical properties and above average chemical resistance the cationic polymerization of epoxy monomers using onium salts has been studied extensively [6–13]. Of all the different types of epoxies, cyclo-aliphatic epoxides have been found to undergo cationic polymerization at the highest rates of any epoxide monomers [11].

The cyclo-aliphatic epoxide, 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate, was selected here for the study of the effect of temperature and an alcohol, 1,6-hexanediol, on its reaction kinetics. For the sake of brevity this epoxy is referred to hereafter as epoxy 3,4. In earlier work Crivello and collaborators have shown not only the beneficial effect of temperature on the cure rate of epoxy 3,4 systems but also the enhancing effect of alcohol monomers on accelerating the epoxide's ring-opening [14]. One experimental difficulty in the aforementioned work is that IR spectroscopy was employed to determine reaction rates with no means to eliminate any temperature rise resulting from the evolution of heat during cure. Hence, the temperature of a sample held between glass slides can increase significantly when irradiated and thereby, make it difficult, if not impossible, to compare the kinetic response of one reactive system to another even though they have the same starting temperature since they could go to two quite different temperatures depending on the quantity of heat released during irradiation (the possible magnitude of this temperature difference will be illustrated later in this paper).

The problem of internal heating causing large temperature increases during the UV curing of epoxy 3,4, was eliminated recently by using a power compensated, photo-differential scanning calorimeter, PDSC [15, 16]. With this instrument the sample temperature can be maintained isothermally independent of the heat evolved during polymerization. Olsson and co-workers' PDSC results on epoxy 3,4 show that during UV irradiation within 25°C of room temperature only single digit conversion levels were achieved before the reaction slowed significantly. In addition, it was noted that when a film of epoxy 3,4 was cured on a UV conveyor belt system under ambient conditions the film was only 7% converted but continued to react in the dark for at least 20 hours under ambient conditions (~23°C). During the dark reaction the film's modulus rose from 0.2 to 1 GPa [16].

Experimental

The epoxy 3,4 monomer, ERL 4221, was purchased from Union Carbide Chemicals and Plastics Corp. (Danbury, CT). The photoinitiator, CyraCure UVI-6974, a triarylsulfonium hexafluoroantimonate, was obtained from Union Carbide and mixed into the epoxy at a concentration of 1 mass%. The alcohol, hexanediol, was acquired from the Aldrich Chemical Co. HD's purity was determined to be 97.71±0.16 mol% from its fusion curve that was fitted to the van't Hoff equation via Perkin Elmer software [17]. All of these chemicals were used as received.

UV-radiation experiments on the curing behavior of epoxy 3,4 were carried out using a differential scanning calorimeter (Perkin Elmer DSC-7) equipped with an irradiation accessory (DPA7) that was fitted with a 450 W high-pressure mercury lamp from Osram (Germany). The sample chamber was swept with helium at a flow rate of 22 mL min^{-1} during the testing. The UV light was unfiltered. After calibrating the PDSC for isothermal work using the melting point standards of *m*-xylene (*m.p.*=–47.9°C), *p*-xylene (*m.p.*=13.2°C) and indium (*m.p.*=156.6°C). The polymerizations were conducted isothermally at temperatures ranging from –40 to 100°C with samples having a mass of 0.7±0.1 mg. To obtain an even distribution of the liquid sample over the bottom of the aluminum sample pans, a disc of transparent polyvinylidine difluoride was placed on top of the liquid sample and left in place during the measurements [18]. This procedure produced films of relatively uniform thickness that were about 20 μm thick. In addition, the plastic cover diminished the evolution of volatile products from the liquid epoxy. During the typical period of irradiation, the epoxy lost less than 0.10 mass% until the reaction temperature exceeded 80°C. At temperatures above 80°C a patented, hermetic capsule with an UV transparent lid was used [19].

The power output of the xenon lamp was determined by placing an International Light Corp. Model IL 745A UV Radiometer at position just above the DSC sample holder closure. Most exposures lasted for 7.5 min (the shutter opened at 0.5 and closed at 8.0 min) and during this exposure period a sample received a dose of approximately 1.1 J cm^{-2}. Energy profiles of the Xenon lamp used in these studies revealed a large portion of the light energy lies above 380 nm. This longer wavelength radiation can be absorbed and converted to heat by the epoxy resin inside the DSC pan. Thus, a sample that absorbs radiation in the visible and infrared region can have a large but constant exothermic signal when the lamp is on. This exothermic effect can be easily eliminated when a second run with the same sample is subtracted from the first run [18]. This difference technique is used in the isothermal DSC experiments shown in this paper. Conventional DSC measurements of melting and glass transitions were carried out on a DSC-7 as well as a Perkin Elmer Pyris DSC in a manner that is described elsewhere [20]. The latter DSC uses a liquid nitrogen dewar and helium to purge its sample chamber. In this configuration the instrument can reach temperatures as low as –170°C.

The sample's modulus was determined in a three-point bending fixture at frequency of 0.8 Hz and a strain of 0.08% using a dynamic mechanical analyzer (Perkin Elmer DMA-7e). Each sample's dimensions were approximately 1.0×3.4×10 mm (*H*×*W*×*L*).

Results and discussion

A photocalorimetric comparison of the isothermal curing of two ~20 μm films of epoxy 3,4 maintained at 30 and 70°C is shown in Fig. 1. The peak maximum decreased from about 1.8 to 1.2 W g^{-1}, as the reaction temperature was increased by 40°C. We assume the exothermic peak is a direct measure of the maximum polymerization rate [21]. Note that the time to reach the maximum polymerization rate is extended from 6 to nearly 50 s as the UV curing temperature rose from 30 to 70°C. Also, the curing exotherm broadened six fold as the temperature of cure was shifted upwards by 40°C. This enlargement of the curing exotherm manifests itself in an increase in the amount of heat released during curing. The apparent heat of reaction, $^{*}\Delta H_{\mathrm{rxn}}$, was obtained by integrating the exothermic curves in Fig. 1 and is equal to – 46 and –192 J g^{-1} at 30 and 70°C, respectively. In this case the degree of conversion, ξ, as a function of time was calculated by dividing $^{*}\Delta H_{\mathrm{rxn}}$ by the heat of reaction, ΔH_{rxn}. The latter value was –664 J g^{-1} based upon a value of –20 kJ mol^{-1} per epoxy group polymerized. Note that at curing temperatures of 30 and 70°C, ξ, multiplied by 100 equals 7 and 29% conversion, respectively.

At 50°C and lower $^{*}\Delta H_{\mathrm{rxn}}$ values of 60 J g^{-1} or lower were observed (Fig. 2). These relatively low reaction rates are equivalent to single digit levels of conversion and remained so until the reaction temperature was raised above 50°C and then the amount of liberated heat was observed to increase dramatically. Separate DSC dynamic scans on these partially cured films revealed that T_g always remained at least 40°C below the reaction temperature as long as the sample temperature remained at 50°C or lower. Hence, this significant slow down in reaction rate is not due to a diffusion controlled process interfering with the chemical reaction [22, 23].

At temperatures above 60°C the exotherms increased in magnitude, until at 100°C the heat liberated equaled 560 J g^{-1} and the degree of conversion exceeded 80%.

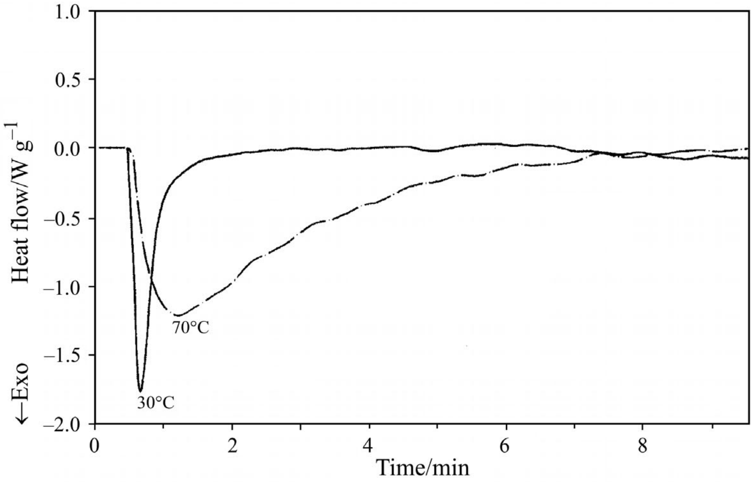

Fig. 1 Exothermic reaction of the UV initiated curing of epoxy 3,4 at 30 and 70°C

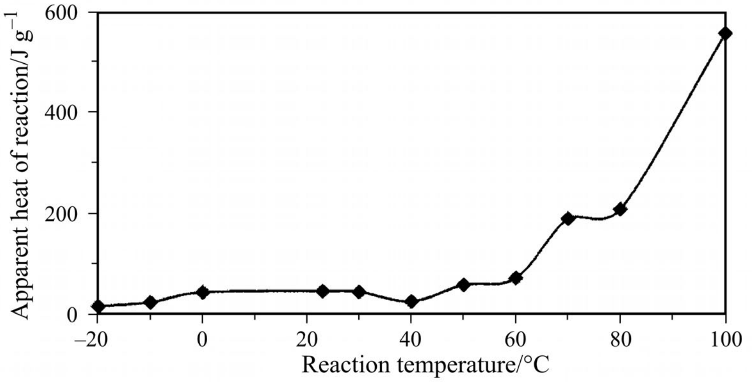

Fig. 2 Apparent heat of reaction of epoxy 3,4 as a function of reaction temperature

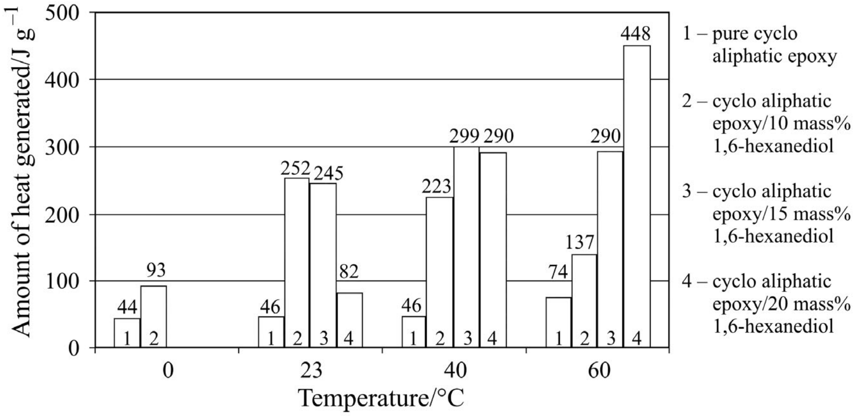

Fig. 3 Heat liberated during the polymerization of epoxy 3,4 and the epoxy blended with 10, 15 and 20 mass% HD at temperatures ranging from 0 to 60°C

At 40°C the heat evolved, $^*\Delta H_{\mathrm{rxn}}$, during UV curing of epoxy 3,4 mixed with 10 mass% HD increased five fold over the value found for epoxy 3,4 alone or from -46 J g^{-1} without the alcohol to -223 J g^{-1} with it present. In addition, at this same temperature the maximum rate of polymerization increased from 1.4 to 5.0 W g^{-1} when the alcohol was added as compared to its not being present. In Fig. 3 the apparent heat of reaction *vs*. the isothermal reaction temperature is plotted for epoxy 3,4 and the epoxy blended with 10, 15 and 20 mass% HD. Note that the presence of alcohol always improved the extent of the reaction but not in a consistent manner with temperature. For example at 23°C epoxy 3,4 blended with 10 mass% hexanediol liberates -252 J g^{-1} but doubling the level of the alcohol to 20 mass% lowered $^*\Delta H_{\mathrm{rxn}}$ to -82 J g^{-1}. However, at 60°C the heat released for 0, 10, 15 and 20 mass% HD blended with epoxy 3,4 was -74, -137, -290 and -448 J g^{-1}, respectively. In Figs 4 and 5 the conversion as a function of the time of irradiation is

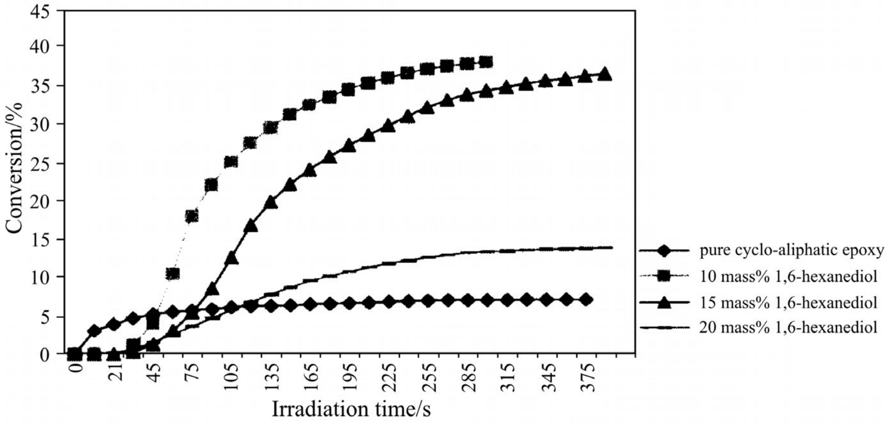

Fig. 4 Conversion *vs*. irradiation time at 23°C for epoxy 3,4 and three alcohol blends with 10, 15 and 20 mass% HD

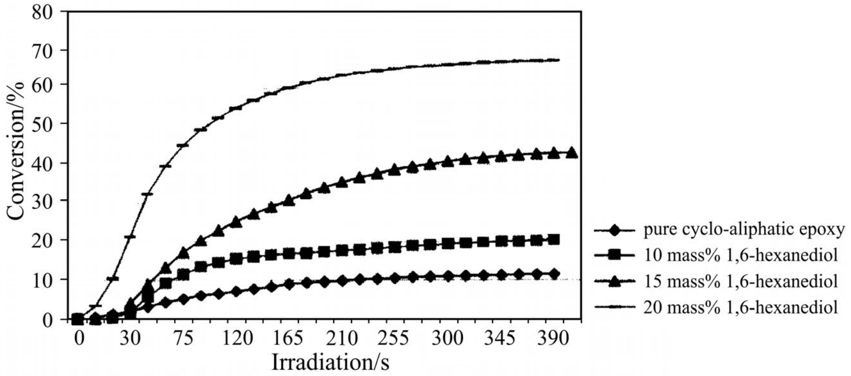

Fig. 5 Extent of reaction plotted *vs*. irradiation time at 60°C for epoxy 3,4 and three alcohol blends with 10, 15 and 20 mass% HD

plotted at 23 and 60°C for epoxy 3,4 and HD blends containing 10, 15 and 20 mass%. To understand this puzzling curing behavior it was necessary to examine the phase behavior of blends of the alcohol with epoxy 3,4 as a function of temperature.

When a HD/epoxy 3,4 (10/90 mass%) blend was quenched at 150°C min^{-1} from the melt to –140°C and reheated at 15°C min^{-1} a small step increase in C_p was observed near –110°C (Fig. 6). This thermal event is due to the glass transition associated with amorphous hexanediol that was created by quenching the alcohol epoxy blend. Subsequent scans of quenched blends containing 5, 15 and 20 mass% 1,6-hexanediol support this contention. In Fig. 7 the DSC scans show that the magnitude of this transition increases in proportion to the amount of alcohol in the blend although the transition temperature remains unchanged. At –60°C a second T_g appears that is associated with epoxy 3,4 followed by the onset of HD's crystallization near –30°C (Fig. 6). The T_g of epoxy 3,4 with no alcohol present is –58°C. The 2°C lowering of epoxy 3,4's T_g indicates that a small amount of mixing of HD with epoxy 3,4 has occurred.

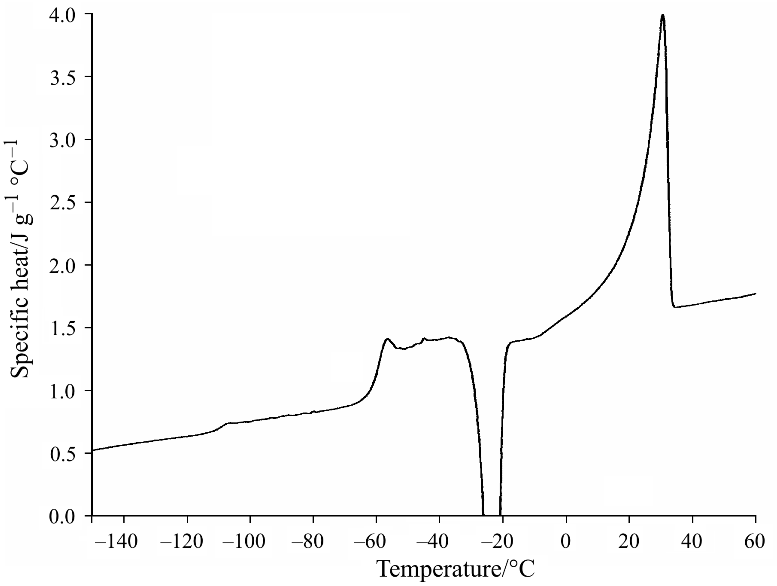

Fig. 6 C_p as a function of temperature for 1,6-hexanediol/epoxy 3,4 (10/90 mass%)

From the onset of HD's crystallization at –30°C the process continues upwards in temperature to its terminus near 0°C with the liberation of –21.5 J g^{-1}. Immediately after the end of crystallization the melting of the newly formed HD crystals began. Between 0 and about 34°C HD crystals melted with the absorption of 21.5 J g^{-1}. Since the apparent heat of crystallization equals that of melting, one may infer that the quenched sample at the start of the scan is completely amorphous. The scan of 97.7 mol% pure, quenched 1,6-hexanediol (Fig. 7) showed no sign of a glass transition or cold crystallization but yielded a sharp melting transition with a melting temperature, T_m, of 40.8°C. The melting process terminates near 50°C with a heat of fusion, ΔH_f, equal to 224 J g^{-1}. The melting temperature of the blend was lowered about 10°C by the diluent effect of the epoxy 3,4 on crystalline 1,6-hexanediol.

The scans of quenched blends of 1,6-hexanediol and epoxy 3,4 show that the melting temperature of the alcohol crystals decreases as the amount of alcohol in the blend is lowered (Fig. 7). The melting peak is located at 25, 31, 36 and 43°C for samples with 5, 10, 20 and 100 mass% HD, respectively.

Note also that as the amount of HD in the blend increased that not only is a higher temperature required to melt HD crystals but also more heat is needed ranging from 11 to about 45 J g^{-1} for blends with 5 and 20 mass% alcohol, respectively.

Blends with 20 mass% HD crystals present had to be heated beyond 50°C in order to melt the HD crystals completely and enable the alcohol to participate in the polymerization whereas blends with 10 mass% HD crystals only needed to be heated to about 30°C to free the HD that is trapped in a crystalline state. Apparently it is this extra quantity of heat at higher temperatures that is required by the HD blends with

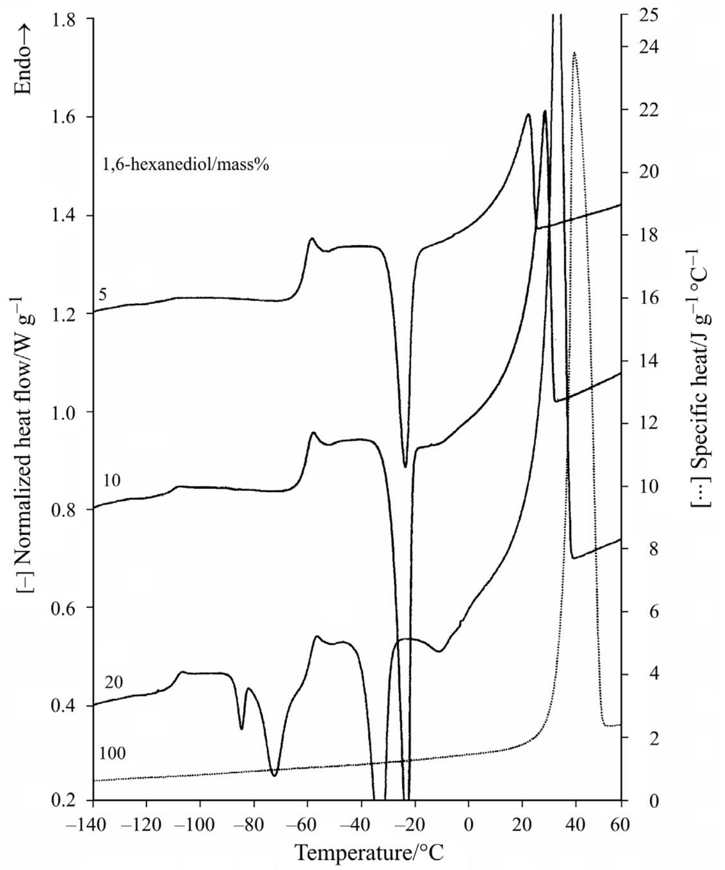

Fig. 7 DSC scans comparing the thermal behavior of quenched samples of HD/epoxy 3,4 with the C_p of 1,6-hexanediol (note the heat flow scans are shifted along the *x*-axis for clarity)

higher alcohol concentrations that explains why the sample with 10 mass% HD reacts more completely at 23°C than the film containing 20 mass% HD.

In a separate experiment the magnitude of the internal heating of a sample was demonstrated on a practical scale. Two samples, each weighing 0.1 g, were enclosed between glass slides with a 1 mm gap. The first had epoxy 3,4 and the second contained a HD/epoxy 3,4 blend (10/90 mass%). The samples were polymerized with the same level of irradiation, namely 1200 mJ cm^{-2}, on a conveyor belt under ambient conditions. The temperature profile of each sample was monitored via a thermocouple, as it moved on the conveyor belt. The epoxy 3,4 sample briefly reached a temperature maximum of about 50°C during the polymerization while the alcohol blend attained a peak temperature of nearly 130°C.

Although blends of HD with epoxy 3,4 accelerated the rate of reaction it also caused the epoxy's ultimate T_g to be decreased as the level of alcohol was raised

(Fig. 8). Note that when the amount of 1,6-hexanediol in blends of epoxy 3,4 reached 30 mass% the glass transition temperature is 18°C. The ultimate T_g for fully cured epoxy 3,4 is 187°C.

The impact of the dark reaction on the modulus of epoxy 3,4 with and without alcohol was monitored. 15 min after a 1 mm thick specimen of epoxy 3,4 was belt irradiated its storage modulus equaled 0.2 GPa. During the initial 200 min of dark aging the epoxy 3,4's modulus increased rapidly as shown with the dash-dot line in Fig. 9. Simultaneously the sample's loss modulus showed a maximum after about 200 min of aging in the dark at 23°C. This result indicates that T_g for this film equaled the ambient reaction temperature at this time. The mechanical loss data sup-

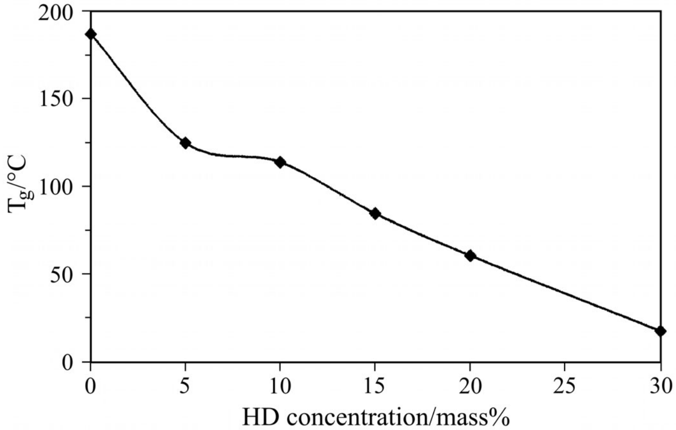

Fig. 8 Glass transition temperature *vs*. the level of 1,6-hexanediol in blends with epoxy 3,4

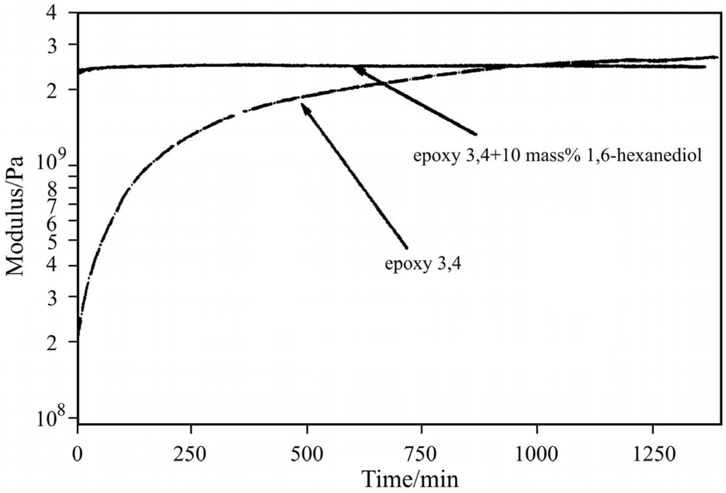

Fig. 9 Comparison of the modulus development of previously irradiated epoxy 3,4 and a blend of it with 10 mass% HD as a function of dark reaction time at 23°C

ports the DSC results showing that after 240 min of aging in the dark T_g was at 23°C. As the T_g of the material reached the sample temperature, molecular diffusion became more difficult and the speed of the reaction was reduced significantly [22–25]. The glassy epoxy's modulus continued to increase slowly until after 1300 min of aging it reached a value of about 2.8 GPa. After room temperature irradiation, a HD/epoxy 3,4 (10/90 mass%) blend's modulus was already at 2.3 GPa or more than ten times greater than was found for the epoxy without any alcohol (solid line, Fig. 9). Additional aging for 1300 min in the dark only raised the blend's modulus by 9% to 2.5 GPa. Thus, the addition of HD to epoxy 3,4 can eliminate the need for dark aging to develop fully a film's modulus under ambient conditions.

Conclusions

Temperature and the presence of an alcohol can have a marked effect on the photoinitiated cationic polymerization of a cyclo-aliphatic epoxy. In isothermal photocalorimetric measurements from 0 to 50°C the level of epoxy 3,4's conversion is less than 10%, even though the T_g of the partially reacted epoxy is as much as forty degrees below the reaction temperature. However, at temperatures above 50°C the extent of reaction begins to increase significantly until at 100°C the degree of cure exceeds 80%. At 23°C adding 10 mass% 1,6-hexanediol to epoxy 3,4 causes the conversion during UV curing on a conveyor belt system to quintuple over the level obtained without the alcohol present. The heat liberated from a hexanediol/epoxy (10/90 mass%) blend caused the sample's temperature to increase by about 100°C above ambient whereas the epoxy alone under these same conditions only experiences a modest temperature rise of approximately 26°C. Increasing the amount of hexanediol in the blend above 10 mass% resulted in decreasing the heat of reaction due to the alcohol being trapped in a non-reactive crystalline phase. However, boosting the reaction temperature above 50°C melts all the HD crystals and thereby, enabled significant improvements in the epoxy's degree of conversion. The glass transition temperature of the 1,6-hexanediol/epoxy blends was found to decrease as the concentration of alcohol blended into epoxy 3,4 was raised and when the amount of alcohol in the blend reached 30 mass% T_g dropped below room temperature.

* * *

This work is dedicated to Prof. Frank E. Karasz on the occasion of his 70th birthday for his many contributions to the field of polymer science. One of us, namely Harvey Bair, was fortunate to have Frank as his mentor when he was a research training fellow at GE Research Laboratory in Schenectady, NY during the early 1960s.

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