

THERMAL CHARACTERISTICS OF THERMOSETS FORMED BY FREE RADICAL PHOTOCURING

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Thermal analysis (TA) is useful for studying the reaction and thermal properties of free radical cured photopolymers. Starting with reactive liquid monomers, the photocuring reactions are initiated by the interaction of UV radiation with an added photoinitiator to form free radicals. The monomers generally are acrylates or methacrylates. Some of the important characteristics of these systems that can be illustrated by TA methods are: 1) the polymers are heterogeneous with more than one phase present even when only one monomer is involved; 2) because of this heterogeneity they have unusually broad glass transitions; 3) the degree of conversion achieved in many UV cured systems is in the 60–80% range, so that considerable residual monomer is often present; 4) partially cured, vitrified samples contain trapped free radicals that will continue to react slowly; 5) when a partially cured photopolymer is heated above its current T_g a reaction exotherm is evident.

Some other aspects of photocuring are not easily disclosed by thermal analysis. Studying fast photoreactions by DSC may not give valid kinetic data because the reaction occurs faster than the DSC instrument time constant. Optical methods (IR, Raman) can be used to advantage in such cases. While photocuring resins are usually exposed to light at ambient temperatures, the local temperature in the resin will be quite elevated, resulting in T_g values that are much higher than ambient. This has been demonstrated by thermal modeling of the reaction and verified by infrared thermography.

Keywords: glass transitions of photopolymers, photopolymer phase heterogeneity, thermal analysis of photocuring

Introduction

Cross-linked polymers formed by UV photocuring are a class of thermosets whose reaction and thermal characteristics can be determined by thermal analysis methods. A majority of UV curing reactions involve cross-linking of unsaturated monomers by a free radical mechanism. The monomers are generally acrylates or methacrylates. These reactions are facilitated by soluble photoinitiators added in small amounts to the monomers. The photoinitiators are light sensitive compounds that decompose on irradiation to generate the free radicals that then initiate the polymerization. The reactions will proceed without any external heat input. Since no heat is supplied, the usual assumption is made that the reactions proceed at ambient temperature. However, the T_g values observed for these polymers are much greater than ambient. For this reason it is often stated that photopolymers differ from ‘normal’ thermosets in that the partially cured systems have T_g values considerably greater than the cure temperature.

In this paper we review some of the important characteristics of photopolymers as elucidated by thermal analysis and thermal modeling. Some of the features of these systems that can be illustrated by TA methods are: 1) the polymers are heterogeneous with

more than one phase present even when only one monomer is involved; 2) because of this heterogeneity they have unusually broad glass transitions; 3) the degree of conversion achieved in many UV cured systems is in the 60–80% range due to vitrification, so that considerable residual monomer is often present; 4) partially cured, vitrified samples contain trapped free radicals that will continue to react slowly; 5) when a partially cured photopolymer is heated above its current T_g a reaction exotherm is evident.

Some other aspects of photocuring are not easily disclosed by thermal analysis. Studying photoreactions by DSC may be problematic. It may not give valid kinetic data if the reaction occurs faster than the DSC instrument time constant. Optical methods (IR, Raman) can be used to advantage in such cases. While photocuring resins are usually exposed to light at ambient temperatures, because the reactions are highly exothermic the local temperatures in the resin will be quite elevated. This will result in T_g values that are much higher than expected. In our previous research we have demonstrated this by thermal modeling of the reaction and verified it by infrared thermography. The high T_g values that are observed thus are consistent with the usual behavior in all thermosets, where the partially cured T_g is approximately the actual cure temperature.

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Results and discussion

Characteristics of photopolymers relevant to thermal analysis and thermal modeling

Photopolymers are heterogeneous with more than one phase present even when only one monomer is involved. Because of this heterogeneity they have unusually broad glass transitions

DSC [1–3] and DMA [4, 5] data for reactive acrylate monomers show clearly that two major phases are present in partially cured photopolymers. This is evident from the appearance of two DMA loss dispersions (Fig. 1) and two T_g s found in DSC curves (Fig. 2). The DMA data of Fig. 1 are for a three-component mixture, containing two multifunctional acrylate monomers and *n*-vinyl-pyrrolidone. In this case the phase heterogeneity results in part from incompatibility that develops during polymerization and in part from the nature of

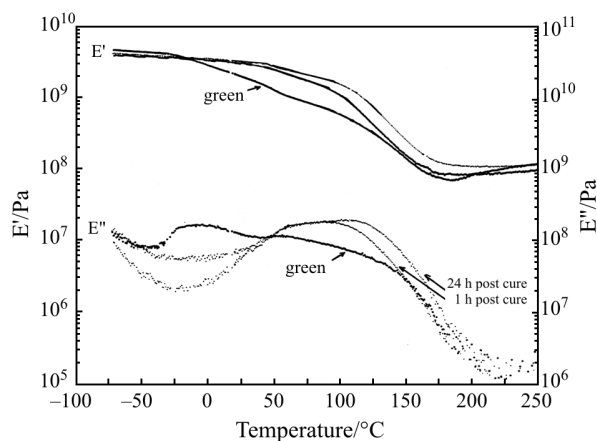


Fig. 1 Sequential DMA plots of storage and loss modulus vs. temperature. Effect of UV post-cure on viscoelastic properties of resin XB 5081. Green sample is initial laser cured; 1 and 24 h samples are green samples subsequently postcured by high-intensity UV lamps

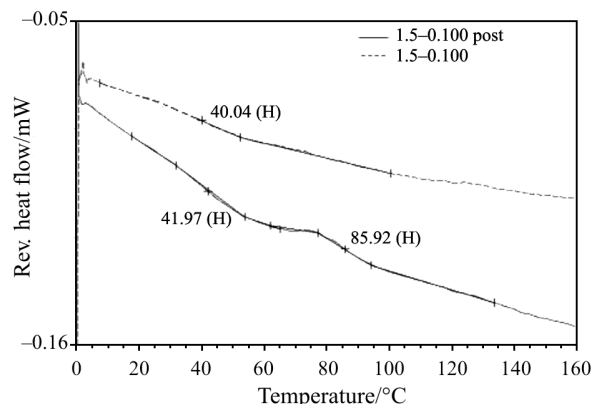


Fig. 2 Sequential MDSC reversing heat flow curves for hexanediol-diacrylate (HDODA) cured with single UV exposure (above) and postcured with second exposure (below); two T_g s are evident in second scan

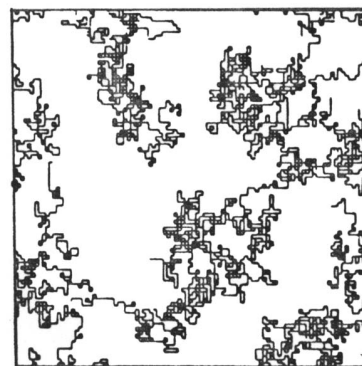


Fig. 3 Graphical representation of results of Monte Carlo simulation for photopolymerization of HDODA monomer showing nonuniform density of cross-linking in partially cured resin; (from J. G. Kloosterboer, *Macromol. Chem. Macromol. Symp.*, 24 (1989) 223)

the polymerization process itself. The data of Fig. 2 for the single component hexanediol-diacrylate (HDODA) speak to the latter factor.

In a single component system the phase heterogeneity results entirely from the statistical nature of the chain polymerization process, and the random coil conformation of the growing chains as well as the increased reactivity of dangling acrylate groups arising from monomer units already attached to the network. It is consistent with the percolation model forwarded by Kloosterboer *et al.* [6–9] (as illustrated in Fig. 3). The simulation data in Fig. 3 indicate that for a single monomer (HDODA) both low and high cross-link density regions develop even at low conversions. The high-density phase consists largely of fairly rigid cross-linked material and the low-density phase is monomer swollen gel. The amount of the high-density phase increases as the polymerization proceeds. This phase has a high T_g , while the low density phase has a low T_g . Figure 1 also shows that the two distinct loss dispersions shift as the degree of conversion advances. The low temperature dispersion advances in temperature, is progressively reduced in intensity, and is absorbed into the high temperature loss dispersion. Also the high temperature (major) dispersion shifts slightly to the right and increases in breadth. The major loss dispersion covers an unusually wide temperature range, indicating that the cross-link network is quite micro-heterogeneous. Additional data on phase heterogeneity during cure in such systems have been cited in other publications [10, 11].

The degree of conversion achieved in many UV cured systems is in the 60–80% range due to vitrification, so that considerable residual monomer is often present

This is illustrated by the time sequence DSC data of Fig. 4 [4, 5]. Here we have three thermal scans of the same partially cured photopolymer depicted in Fig. 1.

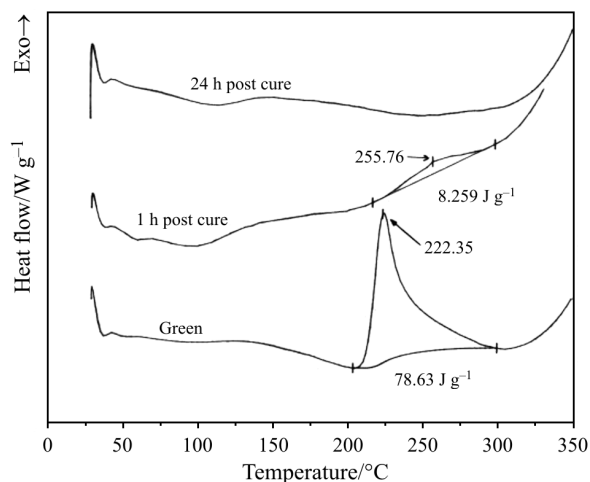


Fig. 4 Time sequence DSC curves for resin XB5081 corresponding to DMA data of Fig. 1

The initial scan is data developed from a laser exposure of a sample at 325 nm [to vitrification at a specified UV dose (time and intensity)], such that the sample is partially cured. The sample was then exposed to a high intensity UV postcure for 1 and 24 h resulting in the 2nd and 3rd scans shown. The high temperature (residual) exotherm corresponding to the thermal cure of residual monomer is initially large but decreases as cure advances due to the increase in conversion during postcure. The kinetic data of Fig. 5 were taken for an acrylate monomer by a reflectance-real time (dispersive) infrared method (RRTIR, discussed below). As indicated the conversion reaches a plateau value at levels much less than 100% due to vitrification under the imposed cure conditions.

Further evidence of the presence of residual monomer may be derived from TG. Figure 6 [2] shows a series of TG curves developed for one sample of un-reacted HDODA, three partially cured samples of HDODA, and one partially-cured sample of a commercial silica-filled HDODA, OG 103-53 (Clariant

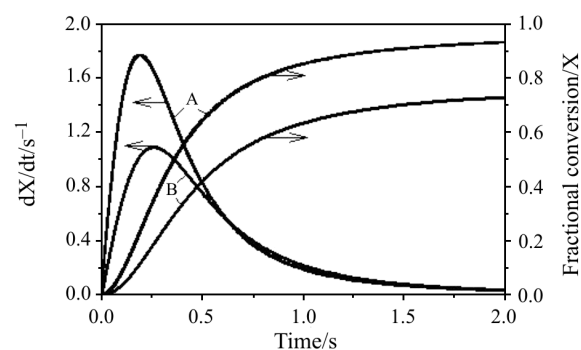


Fig. 5 RRTIR results (infrared kinetic data) for an acrylate monomer containing 0.5% photoinitiator Irgacure 389 A – 100°C, B – 85°C; 363.8 nm irradiation with argon-ion laser, N₂ atmosphere

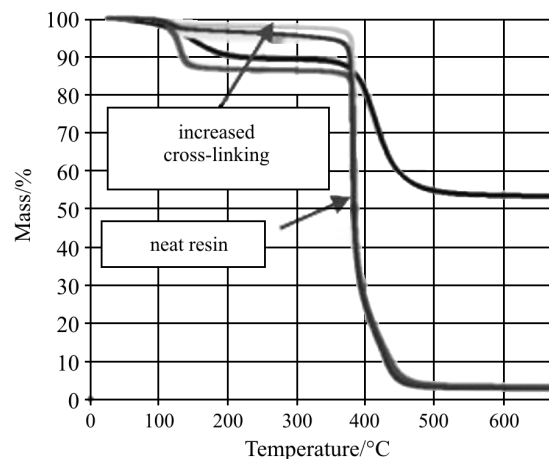


Fig. 6 TG mass loss curves for a series of HDODA samples with increasing cross-link density. Lowest curve is for un-cross-linked monomer, those with increasing mass% plateaus are UV cured samples with progressively higher cross-linking; deep blue sample contains 52% filler; heating rate 5°C min⁻¹; N₂ atmosphere

Corp. Muttentz, Switzerland), which contains 52 mass% nano-particulate silica. Samples were heated at 5°C min⁻¹ in nitrogen. Radiation doses and mass loss data for these samples are summarized in Table 1. The description for the dose of UV radiation given to individual samples is:

$$\text{dose} \equiv \text{time of exposure [s]} \oplus \text{UV intensity [W cm}^{-2}\text{]}$$

For example, a sample given a dose of 1.5–0.100 was exposed to UV for 1.5 s at 0.100 W cm⁻².

In all cases amounts of residual monomer are evolved above T_g in the temperature range of 80–180°C ranging from 1.6 to 12.95%, decreasing in accordance with the increasing degree of cure. Thus, more volatilization is observed in under-cured samples. The amounts evolved correlate with the initial degree of conversion (or cross-linking). As the overall degree of conversion increases, the amount of residual monomer evolved decreases. This is indicated by a decrease in mass loss in the plateau region of the TG curves.

Table 1 Mass loss and corresponding temperatures given by TG

Cure conditions time/s+intensity/W cm ⁻²	$T_{\text{range}}/^{\circ}\text{C}$	Mass loss/%
Uncured HDODA	90–180	12.95
HDODA+silica (52 mass%)	80–220	10.50
HDODA 1.0–0.5	90–170	4.537
HDODA 0.8–1.5	80–150	2.788
HDODA 0.3–3.0 plus 10.3–2.0	90–150	1.623

Partially cured, vitrified samples contain trapped free radicals that will continue to react slowly over an extended time period. These radicals are long lasting. When a partially cured photopolymer is heated above its current T_g a reaction exotherm is evident

The DSC data of Fig. 4 [1–3] in each case show an exotherm when the sample is heated above the low-density phase T_g (refer to discussion above). This is related to additional reaction commencing due to

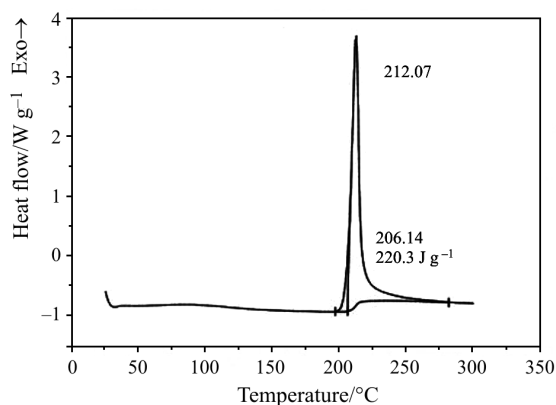


Fig. 7 DSC curve for thermal polymerization of resin XB5081 at $10^{\circ}\text{C min}^{-1}$ in N_2

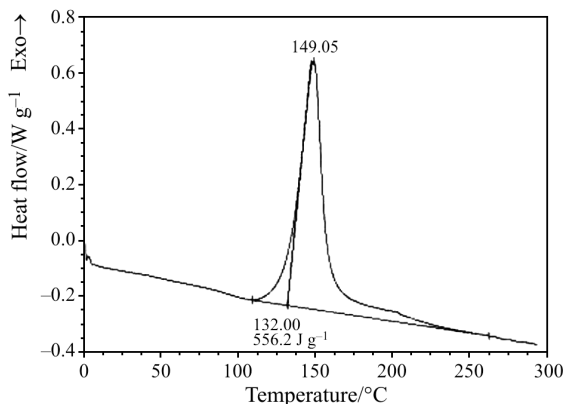


Fig. 8 DSC curve for thermal polymerization of neat HDODA monomer at $10^{\circ}\text{C min}^{-1}$ in N_2

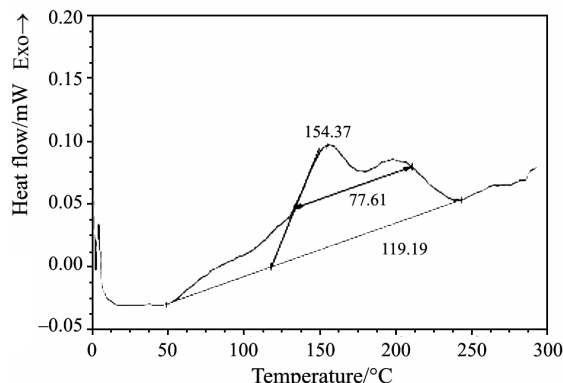


Fig. 9 DSC curve for sample of HDODA partially cured by UV radiation

trapped free radicals. The exotherm is observed at temperatures considerably below the thermal cure temperature of the neat monomer itself (which is over 200°C ; a DSC curve for thermal cure of the neat monomer is shown in Fig. 7). We see a similar situation for the case of HDODA [1, 2], where the thermal reaction of the neat monomer occurs in the range of $110\text{--}240^{\circ}\text{C}$ (Fig. 8). However, on heating a photocured, partially reacted sample of HDODA, an exotherm appears at 50°C due to the reaction of residual monomer with trapped free radicals (Fig. 9). 50°C is slightly above the T_g of the low-density phase swollen with monomer. The presence of trapped free radicals in partially cured acrylate and methacrylate polymers and their decay has been documented in numerous studies by various workers [12–18] using electron spin resonance to directly measure radical populations.

Studying photoreactions by DSC may be problematic. It will not give valid kinetic data if the reaction occurs faster than the DSC instrument time constant

The modified DSC used to study photoreactions is referred to as a differential photocalorimeter, DPC. The time constant of a DPC instrument is at least 2 s. Due to the relatively long response time of DPC, it is not suited for determining, quantitatively, the extent of monomer conversion for fast reactions under high intensity irradiation [19]. Many photoreactions occur in a time frame shorter than 2 s. DPC characterization of such reactions does not fully capture the enthalpy effects that occur, so that kinetic data obtained in such cases are not accurate. Optical methods such as infrared and Raman spectroscopy are more suitable for studying fast photoreactions.

We developed a dispersive IR method for studying fast reactions that is capable of operating at elevated temperatures [19–21]. We refer to this method as real time infrared, RRTIR. It is capable of very short response times and rapid data collection is much better suited for this application, since it can measure reaction kinetics accurately in the millisecond range.

In our laboratory, a comparison was made between RRTIR and DPC in order to determine the extent of the variation in results. In one case, for example, for a specific reaction RRTIR, reveals conversions of 73 and 93% for a given monomer containing 0.5% photoinitiator under continuous laser irradiation at 85 and 100°C , respectively. At the same temperatures, with irradiation of similar dose from a mercury vapor lamp, DPC gave conversion values of 65 and 68%, respectively. It was clear from the data that the short time heat release contribution was missing in the DPC results.

Some thermal analysts maintain that it is possible to circumvent this problem by slowing down a fast

reaction to improve the quantitative results obtained from DPC. However, these reactions are very complex, they invariably involve phase separation, and they are diffusion controlled even shortly after the reaction onset [13, 15–17]. Slowing the reactions down will not duplicate the same conditions that prevail at very short times because of the complex time dependence of the reactions.

Because photopolymerization reactions are highly exothermic the local temperatures in the resin will be quite elevated. This results in T_g values that are much higher than ambient

Measuring instantaneous localized reaction temperatures in photopolymerization is a difficult problem. Flach and Chartoff [22–25] developed a heat transfer model of a photopolymerization reaction triggered by a UV laser beam scanning the surface of a pool of resin. The model effectively simulated Stereolithography (SL), which is a layered manufacturing process where a 3D object is built using a scanning laser to selectively cure the resin. The model clearly indicated that under the normal scanning conditions in SL local temperatures could develop under the laser beam that were in excess of 100°C above ambient. This is due to the intense rapid generation of heat of reaction and low thermal conductivity of the medium and surroundings. Normally photopolymers are formed from thin films flooded by high intensity UV. Under such conditions the local temperatures must be well above ambient. Thus it should be expected that the T_g that develops should be well above ambient and is actually a good indicator of the local temperature rise.

The temperature rise predicted by the model was confirmed experimentally by Leyden and Jacobs at 3D-Systems [26], the manufacturer of Stereolithography equipment, using an infrared thermography temperature measurement device coupled to a video camera. Thus we have well documented video evidence showing the temperature rise and decay along the path of a laser beam that is moving across the surface of a liquid resin and curing the resin as it moves.

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