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Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

STRUCTURE AND MORPHOLOGY OF A POLYETHER/POLYACRYLATE SEMI-INTERPENETRATING POLYMER NETWORK

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Abstract

In this study NMR and DSC are used to probe the structure, thermal characteristics and morphology of a network formed from a diepoxide/acrylate system. Separate chemistries are employed to polymerize the diepoxide and acrylate components. The cationic polymerization of the diepoxide exhibits excellent selectivity in producing a crosslinked polyether network without affecting the acrylate monomer. Subsequent photoinitiated free-radical polymerization of the acrylate produces a phase separated, semi-interpenetrating polymer network (SIPN).

Keywords: cationic and photoinitiated polymerization, DSC, interfacial mixing, interpenetrating polymer network (IPN), glass transition temperature, NMR, quantitative thermal analysis of phases, reactive epoxy and acrylate systems, T_g broadening

Introduction

Interpenetrating polymer network (IPN) systems are defined as an intimate combination of two polymers both in network form, at least one of which is cross-linked in the presence of the other [1–3]. In our earlier work on cross-linked resins containing acrylate monomer, a system based on a vinyl siloxane network was found to have poor selectivity in forming the crosslinked network, resulting in the simultaneous polymerization of significant amounts of the acrylate monomer. A second system based on a diepoxide oligomer exhibited much greater selectivity and is utilized in this current work to form the network that is highlighted in this current investigation.

In this study an epoxy that can be thermally activated is mixed with a photoactive acrylate monomer and the two components reacted in a sequential fashion. First, the blend is heated causing the epoxy to react forming a cross-linked network. Second, the acrylate is exposed to visible light initiating polymerization of the acrylate into linear chains. The resulting structure is termed a semi-interpenetrating polymer network (SIPN).

In this paper we present a description of a modified diepoxide/acrylate system, an analysis of the polymerization chemistry, and a discussion of the thermal characteristics and morphology of the resultant SIPN.

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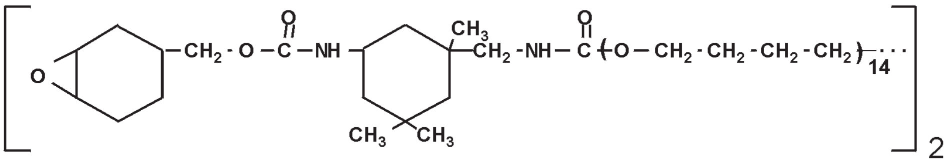
Experimental

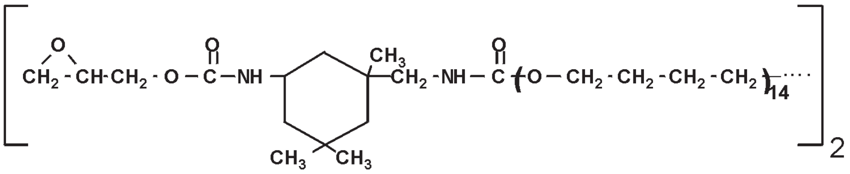
Materials

The diepoxide oligomeric resin, poly-THF-diisophorone-dicyclohexaneepoxide (PTDD),



was prepared by sequentially reacting the endgroups of Terathane® 2000 polyether glycol with isophorone diisocyanate and 3,4-epoxycyclohexylmethanol, which had been prepared by metachloroperbenzoic acid oxidation of cyclohex-3-enylmethanol. Dibutyltindilaurate was used as catalyst in the isocyanate reaction. The resultant oligomer was mixed with phenoxyethylacrylate (PEA), the thermal initiator trimethoxyboroxine, and photoinitator bis(2,6-difluoro-3-pyrrolylphenyl)titanocene (DPPT). The PEA was chosen to provide a high contrast in refractive index between the polyether matrix and the polyacrylate formed by photopolymerization in the data storage process. Curing of the epoxide to the polyether was accomplished at 90°C. Sequential curing of the acrylate was carried out at room temperature with visible light.

The less reactive diepoxide oligomer, poly-THF-diisophorone-dipropyleneoxide (diglycidylether) (PTDP),



was prepared in a manner similar to that used for PTDD but using glycidol to form the glycidyl ether end group. BF_3·etherate was used in place of trimethoxyboroxine as the thermal initiator.

Spectroscopy

NMR measurements were conducted on a Varian Unity 400 Spectrometer. For solid-state experiments, magic-angle spinning (MAS) at 3 and a 55 kHz ^1H dipolar decoupling (DD) field were employed. Carbon spectra were referenced to external, crystalline polyethylene at 33.63 ppm.

Differential scanning calorimetry (DSC)

The phase transition behavior of these materials was studied on a Perkin Elmer Pyris DSC. Baselines were corrected using electronic and software routines. Typically, samples weighed about 10 mg and were heated from below –140°C to about +80°C at 15°C/min. Under these conditions, the temperature gradient in a film is no greater than 0.6°C [4]. The glass transition temperature, T_g, is defined in this work by the half-vitrification temperature. This is the temperature where the endothermic increase, or jump in heat capacity (ΔC_p) due to T_g, is halfway through the transition (i.e., $\frac{1}{2}\Delta C_p$). Note, that the primary output of the power compensated DSC used in this work appears in Figs 5 and 6 in heat flow units (W/g) which scales with C_p. Besides specifying T_g, the extrapolated beginning T_1 and end T_2, respectively, of the glass transition were located by a method that was described earlier [4]. The difference in these latter measurements establishes the width of the glass transition interval, ΔT_g. Quantitative analysis of the amount of material in a separate phase was carried out based on ΔC_p measurements [5].

Results and discussion

Both simultaneous [6] and sequential [7] IPNs from mixtures of the diglycidyl ether of bisphenol A and acrylates have been described. In these examples, amines were used to crosslink the epoxides. The first reaction in forming the sequential IPN was not conducted in the presence of the second monomer. Instead, the second monomer was added after formation of the first polymer network structure. We have examined the possibility of using separate chemistries to form IPNs from the diepoxide/acrylates using cationic polymerization of the epoxides and free radical polymerization of the acrylates. We avoided the use of amines in the curing of the diepoxide oligomer since amines also would be expected to react with the acrylates. The chemistry is designed to provide sequential polymerization of the different monomers with all components of the formulation mixed before any reaction begins.

Cationic polymerization of diepoxide

In earlier studies we examined the cure of several diepoxides that varied in molecular weight and chain flexibility [8]. Egger *et al*. [9] have demonstrated that for short chain diepoxides the introduction of a flexibilizer such as polypropylene glycol (PPG) results in a higher conversion of the diepoxide monomer and an increase in the reaction rate. The PPG participates in the polymerization via a chain transfer mechanism that results in placements of the linear propylene glycol chain within the highly branched polyether network. We have found that by placing a long, flexible spacer between the two terminal epoxy groups of the monomer, a highly cured film with a low T_g can be obtained in the presence of plasticizing acrylate monomer. An example is the oligomer PTDD (see structure above).

The relatively high reactivity of the cyclohexaneepoxide of PTDD made control of the diepoxide polymerization difficult, frequently resulting in less than 70% conversion of oligomer to polymer and a cloudy material. The reactivity of this epoxide is such that curing of the PTDD begins as the components of the formulation are being mixed, making it very difficult to obtain a clear, homogeneous mixture. The use of the less reactive, glycidyl ether groups of oligomer PTDP (see structure above), cured at +90°C with BF_3·etherate as catalyst, provided more reproducible results with complete conversion of the epoxides to polyethers and no loss of acrylate monomer. However, optical clarity was still obtained only with difficulty. The compatibility of the PEA and the PTDP is limited. Concentrations of PEA above 25 wt% produce cloudy mixtures but concentrations below ca. 20 wt% result in less than full cure of the diepoxide oligomers because of insufficient plasticization. Mixing of the solid PTDP and liquid PEA/BF_3·etherate must be carried out with some heating but this must be limited or polymerization will begin before the monomer and initiator are uniformly mixed with the PTDP. As a consequence of these issues only about ten percent of the cured samples were homogeneous and exhibited optical clarity.

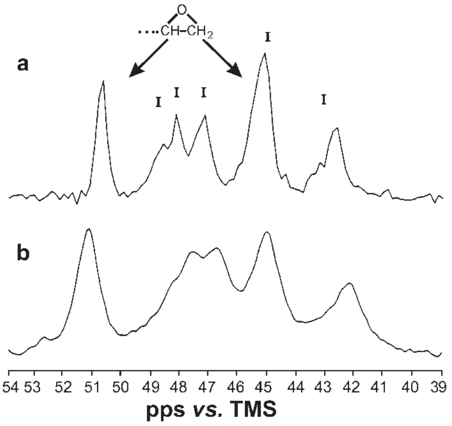
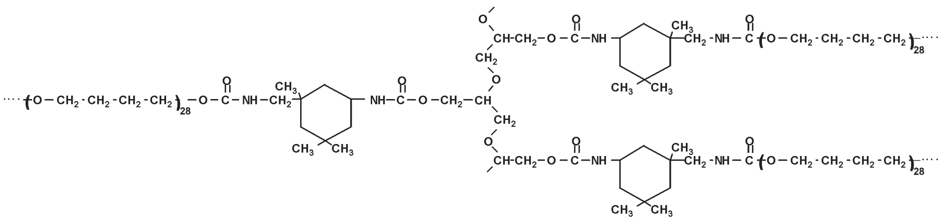


Fig. 1 ^{13}C NMR spectra of a) unreacted PTDP in 1,2,4-trichlorobenzene recorded at room temperature ('I' = isophorone) and b) partially cured (25%) PTDP film recorded with magic-angle spinning and dipolar decoupling at +90°C

The resonances of the methine and methylene carbons in the epoxide structure provide monitoring of the level of reaction during the cationic polymerization. The portion of the ^{13}C spectrum of the unreacted PTDP oligomer containing these resonances, recorded in 1,2,4-trichlorobenzene under quantitative conditions, is presented in Fig. 1a. Since the methylene signal overlaps with a resonance of the isophorone structure, the methine carbon peak is used to measure the level of epoxide reaction. The extent of epoxide cure can be determined by comparing the integral of this resonance to that of the non-reactive $–CH_2–O–$ methylene carbon (72 ppm, not shown) in the polyether mid-block of the oligomer.



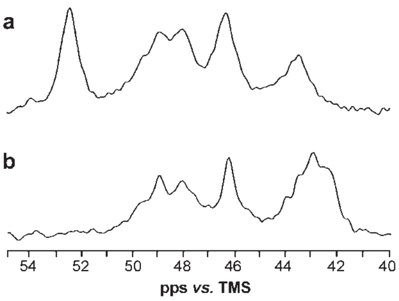
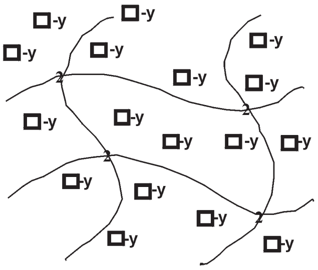


Fig. 2 Solid-state ^{13}C MAS/DD NMR spectra recorded at +90°C for a) partially cured (25%) poly(PTDP) and b) fully cured poly(PTDP)/PEA

As an example of monitoring the cationic polymerization that leads to formation of the polyether network structure, the resonances of the epoxide carbons of a partially cured, neat sample of poly(PTDP) are compared in Fig. 1b to resonances in the solution spectrum of unreacted PTDP. To maximize the resolution of the solid film of poly(PTDP), magic-angle spinning and high power, proton decoupling are employed in recording these NMR data at +90°C. The comparison of integrals of the epoxide CH carbon resonance and the polyether mid-block CH_2O carbon resonance before and after polymerization indicates an epoxide reaction level of 25%. Simultaneous with the loss of signal for the epoxide carbon resonances, new signals representing the polyether structure are observed in the 65 to 68 ppm region (not shown).

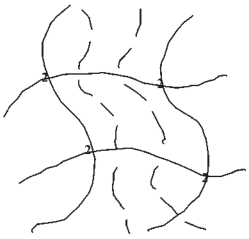
In Fig. 2, the spectrum of the partially cured, neat poly(PTDP) is compared to that of poly(PTDP)/PEA, oligomer cured for 3 h at +90°C in the presence of 25 wt% PEA. The absence of any CH signal intensity at 52 ppm in Fig. 2b demonstrates that the polymerization of PTDP in the presence of the acrylate goes to completion. We attribute the higher level of conversion to the plasticization effect of the acrylate monomer. Since PTDP is difunctional, the polyether formed is a crosslinked network with a low crosslink density due to the large linear polyether mid-block. For the reasons described above, only about ten percent of the samples become clear, solid films. In films that lack observable turbidity, the PEA monomer probably remains miscible in the polyether formed from the PTDP.

The selectivity of the cationic polymerization can be measured by examining the signal strength of the carbonyl resonances of the PEA monomer and its polymerized product, poly(phenoxyethylacrylate) (PPEA). The MAS spectrum for poly(PTDP)/PEA shown in Fig. 3a was recorded at room temperature to avoid additional sample heating beyond that required for polymerization of the PTDP oligomer. The spectrum exhibits the PEA carbonyl resonance at 168 ppm but no signal from that PPEA at 176 ppm. This demonstrates that during the 3 h thermal cure of the diepoxide the PEA does not polymerize. Further, a comparison of integrals for the PEA carbonyl resonance and the ether carbon of the poly(PTDP) midblock indicates that no PEA is lost due to volatilization. The results illustrate that the selectivity of the cationic polymerization is excellent and that the crosslinked polyether network is formed in the presence of unreacted monofunctional acrylate monomer (□-y):



Free-radical polymerization of acrylate

Following polymerization of the PTDP oligomer the resultant film was exposed to 547 nm light for 90 s to initiate free-radical polymerization of the acrylate monomer. After this exposure the sample is irradiated with a broad spectrum lamp for 30 min. The resultant polyether/polyacrylate SIPN material is a very tough, transparent film with a yellow color. A portion of the ^{13}C NMR spectrum of this material is shown in Fig. 3b. A comparison of the integrals for the carbonyl resonances of PEA and PPEA at 168 and 176 ppm, respectively, indicates an acrylate monomer to polymer conversion of 90%. We have not attempted to optimize the photocure by variation of photoinitiator concentration or the reaction temperature. The NMR data demonstrate that it is possible to obtain a SIPN in which free radical polymerized linear polyacrylate is obtained subsequent to cationic polymerization of a diepoxide oligomer.



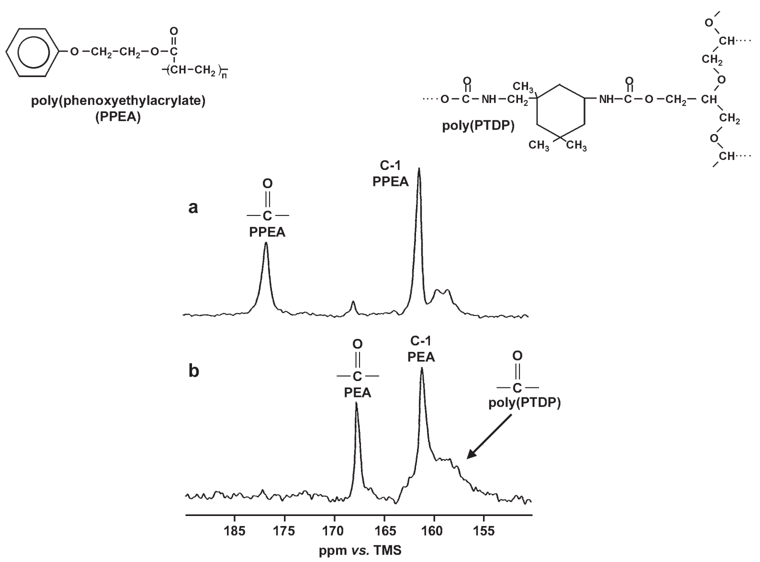


Fig. 3 Solid-state ^{13}C MAS/DD NMR spectra of a) thermally cured poly(PTDP)/PEA recorded at +23°C (PEA = phenoxyethylacrylate) and b) poly(PTDP)/ poly(phenoxyethylacrylate) SIPN recorded at +90°C (PPEA = poly(phenoxyethylacrylate)

Thermal properties of SIPN

To gain some understanding of polymer morphology, the thermal characteristics of the polyether/polyacrylate SIPN as reflected in the DSC data were examined. The results for the SIPN and polyether and polyacrylate homopolymers are shown in Fig. 4.

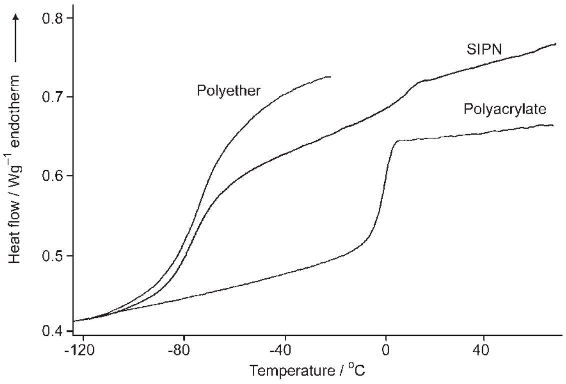


Fig. 4 DSC of poly(PTDP)/poly(phenoxyethylacrylate) SIPN and the corresponding homopolymers: polyether = poly(PTDP) and polyacrylate = poly(phenoxyethylacrylate)

The values of T_g, the breadth of the transitions (ΔT_g), the change in heat capacity associated with each transition (ΔC_p), and the polymer fraction calculated from the ΔC_p are shown in Table 1. The polyacrylate, poly(phenoxyethylacrylate), is a commercial sample that was most probably prepared by dilute solution polymerization. It exhibits a classic glass transition at 0°C with the transition occurring over a narrow temperature range. The polyether, poly(PTDP) polymerized in the bulk, displays a very broad glass transition especially in the high temperature portion. We attribute the broadening to incomplete curing in the bulk that results in a heterogeneous material. The unreacted oligomer produces some crystallization and subsequent melting at higher temperatures and for this reason the DSC trace of the polyether is arbitrarily halted at –20°C. The comparison of T_gs in the homopolymers and SIPN demonstrates that the polyether and polyacrylate portions of the SIPN manifest transitions similar to that of the corresponding homopolymers. The presence of these transitions is interpreted as reflective of a phase separated polymer morphology. As is expected in IPNs [10, 11] the lower transition is shifted to higher temperature. Normally, the higher temperature transition would be displaced toward lower temperature [5]. We attribute the observation of a higher T_g in the polyacrylate portion of the SIPN compared to the polyacrylate homopolymer to differences in polymer structure. Compared to dilute solution polymerization, there is a much higher probability of chain transfer to polymer by abstraction of methine hydrogen in the bulk polymerization of the acrylate monomer in the SIPN. This leads to increased branching and crosslinking that produces a polymer structure with fewer degrees of freedom; such a structure should be associated with a higher T_g.

Table 1 DSC of SIPN and corresponding homopolymers

	T_g/°C	ΔT_g/°C	ΔC_p/J (g °C)$^{-1}$	Polymer fraction
Polyether	–70	30	0.88	100
Polyacrylate	0	10	0.56	100
Polyether in SIPN	–72	21	0.59	67
Polyacrylate in SIPN	5	17	0.16	29

As shown in Fig. 5, the broadening of the T_gs in the polyether/polyacrylate SIPN can be more readily observed by replotting the data with extrapolation of the baseline between shifts in C_p. This broadening is typical for IPNs. Most of the effect is to the high side of the lower temperature transition and to the lower side of the high temperature transition. This shifting and the broad nature of the transitions are ascribed to phase mixing at the interphase region between the phase separated domains of the polyether and polyacrylate portions of the SIPN. This kind of mixing between domains normally leads to enhanced film toughness which is noted here [12]. However, the complete resolution of the two T_gs and the small

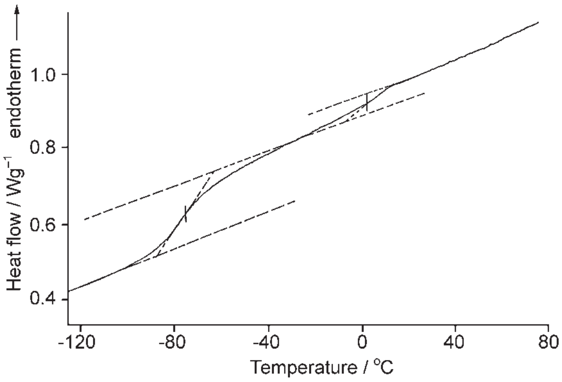


Fig. 5 DSC of poly(PTDP)/poly(phenoxyethylacrylate) SIPN

shift from the values of T_g in the homopolymers suggest that the phase separated domains are large. If we employ the heat capacity data of Table 1 to estimate the fraction of each polymer in the SIPN, we obtain a polyacrylate fraction of 29% and a polyether fraction of 67%, not far from the original composition of 25 wt% acrylate monomer and 75 wt% PTDP. Some difference is expected due to the incomplete reaction of the acrylate.

The observation of clear films for the SIPN indicates that either the domain sizes are very small or the two polymers are fortuitously index matched, i.e., the respective refractive indices of the polymer fractions are so closely matched ($^{\delta}$n estimated at ~0.03) that the film appears clear despite a large scale, phase separated morphology. Since the DSC data suggest large domains, we think the probability of index matching is high.

Although the SIPN described in this work appeared as a clear film that is mechanically very tough, in most preparations the SIPN film suffers from poor optical clarity. This results from a large sensitivity to the concentrations of the acrylate monomer: too little monomer prevents complete polymerization of the PTDP oligomer, and too much acrylate yields cloudy or opaque films. Attempts to obtain a harder material by raising the glass transition temperature with higher T_g oligomer resulted in an incomplete cure of the oligomer. Optical quality also decreases with the use of higher T_g acrylate monomer. The results of this study clearly demonstrate the difficulty in manipulating and optimizing the optical and mechanical properties of the two-phase morphology in an IPN system produced with separate chemistries.

Conclusions

The cationic polymerization of a diepoxide oligomer at +90°C in the presence of acrylate monomer is selective and forms a crosslinked polyether network. The NMR results show that the polyether network is formed in the presence of the unreacted monofunctional acrylate monomer. The subsequent, free radical polymerization of the acrylate monomer to linear polyacrylate results in a SIPN with phase separated morphology. DSC studies of this SIPN indicate that some mixing has occurred between domains. In addition, quantitative analysis based on ΔC_p measurements yields a phase composition in good agreement with the original composition of 25% polyacrylate fraction and 75% polyether fraction. Although clear but colored films with good toughness can be obtained, most samples are cloudy and optical quality is difficult to control.

* * *

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