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Analysis of phase mixing in aged polymer networks of poly(ethylene glycol) and poly(trimethylolpropane triacrylate)

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The extent of phase mixing during ageing of semi-interpenetrating polymer networks of poly(ethylene glycol) (PEG) and poly(trimethylolpropane triacrylate) (TMPTA) was determined using differential scanning calorimetry. Twelve-month-old networks containing PEG with molecular weights of 8000–20 000 g mol^{-1} were more phase-separated following ageing than freshly prepared networks, while other PEG molecular weight (4000 or 100 000 g mol^{-1}) systems remained stable. The networks initially formed with fast TMPTA gelation rates remained phase-stable, while those which were initially formed with progressively slower TMPTA polymerization kinetics became more phase-dispersed upon ageing.

(Keywords: IPN; ageing; phase stability)

INTRODUCTION

Recently, we prepared and characterized semi-interpenetrating polymer networks (semi-IPNs) of PEG and TMPTA which were synthesized from the polymer-in-monomer melt[1]. Molten PEG and TMPTA monomers were miscible up to a PEG mass fraction of 40%, as measured by isothermal calorimetry. Therefore, any observed phase separation in the final network was attributable to polymer incompatibility and PEG chain aggregation from the growing TMPTA matrix. Polymer phase mixing was determined using differential scanning calorimetry (d.s.c.) in order to measure the amount of the crystalline PEG phase, while the physical dimensions of the phases were measured using transmission electron microscopy (TEM).

The extent of phase mixing of these thermodynamically unstable semi-IPNs was postulated to be a superposition of chemical processes (rate of TMPTA gelation to raise network viscosity and kinetically entrap the PEG component) and physical processes (mass transport of the PEG chains to aggregate and phase separate). The balance of these two processes determined the phase mixing of the final network.

Because these networks contained physically entrapped PEG (with the exception of those containing α,ω-diacrylate functionalized PEG (PEGDA)), it is possible that the mixing of the PEG component may be kinetically unstable over long periods of time. PEG is a highly flexible and mobile molecule[2] with a low glass transition ($\sim -70^{\circ}$C); this molecular mobility may enable the PEG phase to become more crystalline or to phase separate further so as to grow in dimensions. As larger chain dimensions have limited mass transport properties, the stability of phase mixing may be dependent upon the molecular weight. In addition, if the TMPTA crosslinking density is low, then spontaneous PEG segregation may also commence. For example, the phase stability of poly(methyl methacrylate)/poly(carbonate–urethane) (PMMA/PCU) or PCU/polystyrene (PS) networks may be partially dependent upon molecular weight or crosslink density[3]. Simultaneous IPNs of PMMA/PCU containing 70% mass fraction of linear PMMA spontaneously phase-separated after 2.5 years, perhaps due to low-molecular-weight PMMA species diffusing from the network. In contrast, semi-IPNs of linear ultra-high-molecular-weight PMMA in crosslinked PCU remained phase-mixed after 2.5 years, due to the limited mobility of the large chains. Semi-IPNs of 15% linear PS in crosslinked PCU remained phase mixed for up to 7 months, while blends of linear PS and linear PCU spontaneously phase-separated due to a lack of crosslinks and reduced permanent physical entanglements[4]. Greater crosslink densities also reduced the chain segmental motion in poly(propylene oxide)/epoxy networks, thus increasing the time necessary for the network to age into a structural equilibrium state when physically stressed[5].

In this note, we examine the kinetic stability during ageing of semi-IPNs of linear PEG in crosslinked networks of TMPTA by using d.s.c. Grafted semi-IPNs, with PEGDA, were also examined. Increases in the melting endotherm with age were used as an indication of enriched PEG phases. Increases in the dimension of the PEG phases with age were qualitatively assessed by changes in the macroscopic appearances of the networks.

EXPERIMENTAL

Materials

PEG (4000, 8000, 10 000, 20 000, and 100 000 g mol^{-1}; $M_w/M_n = 1.13$–1.25; Fluka) was dehydrated by azeotropic distillation in benzene, precipitation from hexane, and drying *in vacuo*. Benzoyl peroxide (BP, Polysciences),

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2,2'-azobisisobutyronitrile (AIBN, Polysciences), and 2,2-dimethoxy-2-phenylacetophenone (benzil dimethyl ketal, BDMK, Aldrich) were used as received. TMPTA (Sartomer) and all organic solvents were dried over molecular sieves (Type 4A, EM Science). PEGDA (4000 g mol^{-1}) was prepared by the end-group alcoholysis of acryloyl chloride (Aldrich), and confirmed by 500 MHz ^{1}H n.m.r. spectroscopic analysis (General Electric), as described previously[1].

Network synthesis

PEG (0.4 g), TMPTA (1.0 g) and BDMK (0.001–10 wt%, on a TMPTA basis) were heated to 100°C (under which conditions the PEG dissolved in the TMPTA monomer), mixed to homogeneity, and then poured between two clean glass coverslips (#1, Corning) separated by a 0.36 mm thick PTFE gasket (Small Parts); the arrangement was then clamped with binder clips, and placed in a prewarmed oven (100°C) equipped with a window. Ultra-violet light from a 100 W Hg vapour lamp (360 nm; UVP) was shone through the window perpendicular to the coverslips until curing was complete, based on curing times that were previously established[1]. Additional networks were synthesized using BP or AIBN (0.3 wt%, on a TMPTA basis) at 100°C, also based on the previously established curing times[1]. TMPTA homonetworks were photopolymerized using 0.3 wt% BDMK. The networks were stored desiccated in darkness at room temperature for twelve months.

Characterization

Differential scanning calorimetry (DSC Series 2, Perkin–Elmer) was performed on aged networks over the temperature range −50 to 200°C at a heating rate of 20°C min^{-1}, and then quenched to −50°C at a rate of 160°C min^{-1}. As the networks themselves were crosslinked, any observed melting endotherms were assigned to the phase-separated PEG component and were normalized to the amount (per gram) of PEG that was present in the semi-IPN. The fraction of PEG that was crystalline (% PEG crystallinity) was calculated as the ratio of the measured melting endotherm, normalized per gram of PEG in the sample, to the measured pure PEG melting endotherm of 180 J g^{-1}.

The heats of polymerization were measured in order to calculate the conversion of TMPTA monomer during polymerization in freshly prepared networks. Heats of photopolymerization were measured using d.s.c. operating in isothermal mode at 100°C with u.v. exposure, while the heats of thermopolymerization were measured using d.s.c. over the temperature range 50–200°C at a heating rate of 20°C min^{-1}. These heats were normalized per mole of TMPTA that was present in the semi-IPN, and the TMPTA conversion was calculated using the value of 86.2 kJ per mol C=C for an acrylate-group addition process[6].

RESULTS AND DISCUSSION

Phase separation in freshly prepared networks

In a summary of previous studies examining the component mixing in PEG/TMPTA networks[1], it was observed that networks were more phase-mixed if the PEG molecular weight was raised, presumably due to the limited mass transport for forming aggregates with larger PEG chain dimensions. Networks prepared under fast TMPTA gelation kinetics were more phase-mixed than if prepared with slower polymerization rates, presumably due to the inability of the slowly growing crosslinked matrix to overwhelm chain aggregation and kinetically entrap the PEG in a non-equilibrium phase-mixed state. Rapidly photopolymerized networks had PEG phase dimensions of 80–100 nm, while slowly thermally polymerized networks had micrometre-sized phases. Networks prepared with PEGDA possessed no TEM-resolvable phases as a result of the chains being covalently grafted into the TMPTA matrix.

Ageing dependence upon PEG molecular weight

The phase stability of the networks was evaluated as a function of the PEG molecular weight (*Table 1*). Networks of low- or high-molecular-weight PEG (4000 or 100 000 g mol^{-1}) were stable after 1 year of storage, demonstrating no increase in the fraction of PEG that was crystalline, while moderate molecular weights (8000–20 000 g mol^{-1}) became more crystalline. These networks not only became more crystalline, but they also became less transparent, suggesting increases in their PEG phase dimensions. Networks with PEGDA remained completely phase mixed with ageing, resulting from the covalent grafting of the PEG chains into the TMPTA lattice.

No correlation was found between the melting endotherms and optical clarity. For example, aged networks containing 4000 and 8000 g mol^{-1} PEG had approximately the same melting endotherms but very different optical clarities. These observations suggest that both networks contained the same percentage of PEG in the separated and crystalline phases, but that the dispersion of the phases was greater for the 4000 g mol^{-1} PEG system.

Differing amounts of PEG phase separation during network formation may result in differing extents of TMPTA conversion and thus a differing response to ageing. The extent of conversion of TMPTA during polymerization was independent of the PEG molecular weight (*Table 1*); however, the potential for the formation of permanent entanglements (per PEG chain) may have increased with higher molecular weights. As resistance of

Table 1 Network ageing as a function of the PEG molecular weight

M_w of PEG (g mol^{-1})	PEG crystallinity (%)		Appearance[a]		TMPTA conversion (%)
	Fresh[b]	Aged	Fresh	Aged	
4000	39 ± 4	39 ± 3	vs tc	vs tc	61 ± 3
8000	28 ± 1	42 ± 3[c]	vs tc	op	60 ± 2
10 000	23 ± 1	33 ± 2[c]	tp	tc	60 ± 1
20 000	13 ± 1	17 ± 2[c]	tp	vs tc	61 ± 3
100 000	13 ± 0	13 ± 2	tp	tp	60 ± 2
PEGDA	0 ± 0	0 ± 0	tp	tp	60 ± 2
TMPTA homonetwork			tp	tp	66 ± 2

[a] Appearance: vs tc, very slightly translucent; tc, translucent; tp, transparent; op, opaque

[b] Results from ref. 1

[c] Changes statistically significant using a one-tailed probability distribution with a 0.10 level of significance

Table 2 TMPTA conversion for networks containing 4000 g mol^{-1} PEG as a function of initiator system

Initiator	Amount (wt%)	TMPTA conversion (%)
BDMK	0.3	61±3
BDMK	0.1	38±3
BDMK	0.01	16±2
BDMK	0.001	–[a]
BP	0.3	65±3
AIBN	0.3	56±3

[a] Too slow to measure

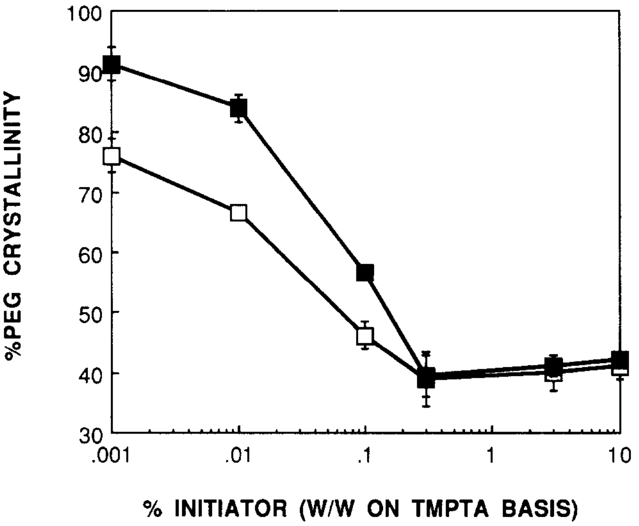

Figure 1 PEG crystallinity change with ageing as a function of initiator concentration. The increase in PEG crystallinity during ageing depended upon the rate of polymerization in network formation, which was determined by the initiator system, shown here as the concentration of BDMK: (□) PEG % crystallinity in freshly prepared networks; (■) crystallinity after ageing for 1 year. Error bars show standard deviations

the networks to solvent extraction or to PEG surface rearrangement may depend upon reptation[1,7], resistance to spontaneous phase separation with ageing may also be reptation dependent. All networks may be demixing with age to approximately 40% PEG crystallinity; the 4000 g mol^{-1} PEG may have spontaneously separated to this extent very quickly, while the 8000 g mol^{-1} PEG material must age to do so. High molecular weights (100 000 g mol^{-1}) may be demixing to this extent immeasurably slowly.

Ageing dependence upon initiator system

Freshly prepared networks made with low photoinitiator concentrations became opaque during polymerization (data not shown) and had low levels of TMPTA conversion (*Table 2*); this suggests that these networks had poor through-cure, as decreased capture during u.v. exposure can lower the ultimate conversion of multiacrylated monomers[8]. Consequently, networks made with low concentrations of photoinitiator were more susceptible to spontaneous PEG phase crystallinity upon ageing (*Figure 1*), and this phenomenon was correlated with a lower crosslink density (i.e. a lower cure extent) in the network.

In comparison to photopolymerization with low concentrations of BDMK, thermally initiated networks also resulted in long TMPTA gelation times and contained large micrometre-sized PEG phases[1]. These networks exhibited high degrees of crosslinking (*Table 2*) and thermally polymerized networks were stable for up to 1 year of storage and demonstrated no or little increases in PEG phase separation or crystallinity (BP 40±2% crystallinity, fresh; 41±2% crystallinity, aged; AIBN 53±1% crystallinity, fresh; 61±1% crystallinity, aged). However, the extents of phase separation in the freshly prepared networks were high, and this feature, rather than the high crosslink density in the TMPTA matrix, may give rise to the stability.

CONCLUSIONS

The stability of non-equilibrium phase-mixed networks of PEG/TMPTA to spontaneous crystallization or coalescence during ageing depended both upon the component molecular weight and the nature of the initiator system. Slowly crosslinked photopolymerized networks were sensitive to spontaneous phase demixing during ageing, while rapidly crosslinked networks were less sensitive, and this was correlated to a low TMPTA conversion. Networks containing PEGs with high molecular weights were stable during ageing, presumably due to a larger number of entanglements per PEG chain and consequently a slower diffusion to form PEG-rich aggregates. The networks that demonstrated very high PEG phase separation during initial network formation were stable after ageing for one year, which was perhaps due to a lower thermodynamic driving force for continued phase separation.

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