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Metastable phase diagrams for simultaneous interpenetrating networks of a polyurethane and poly(methyl methacrylate)

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Phase separation and gelation in simultaneous interpenetrating networks (SINs) are studied for the model system polyurethane–poly(methyl methacrylate) (PU–PMMA). A metastable phase diagram is developed as a tetrahedron in three dimensions in which the four vertices represent the four individual components: the two polymers, PMMA and PU, and the two monomer (or prepolymer) mixtures, MMA and 'U'. The time order of three events, gelation of polymer I, gelation of polymer II and phase separation of polymer I from II, is explored. The tetrahedron constructed represents these three events as curved or planar surfaces going through its volume. The intersections of any two surfaces produce critical curves or lines representing, for example, simultaneous phase separation and PMMA gelation, or simultaneous gelation of PMMA and PU. These are critical conditions capable of playing key roles in the development of an SIN's morphology and hence properties. The metastable phase diagram allows visualization of the course of the three events during SIN synthesis, and provides direction for controlling them with respect to these critical conditions.

(Keywords: interpenetrating networks; metastable phase diagrams; polyurethane)

Introduction

Simultaneous interpenetrating networks (SINs) are a special class of interpenetrating polymer networks (IPNs)[1] which are synthesized by first mixing all monomers or prepolymers with corresponding crosslinkers, before either of the two networks is formed. Thus, a polymerizing SIN system may be considered to be composed of four individual components: two sets of monomers and two network polymers.

In spite of the numerous studies on IPNs and SINs, and their important applications, the amount of literature addressing their phase diagrams remains limited[2]. In part, this is due to their crosslinked structure, which rarely allows thermodynamic equilibrium with respect to phase separation. In a strict sense, therefore, phase diagrams cannot be constructed. In this paper, it is proposed that a metastable phase equilibrium be defined for IPNs and SINs. A possible state of affairs is the condition at which the thermodynamic forces of phase separation are exactly counter-balanced by the mechanical constraints of the network structure. In concept, the magnitude of these mechanical constraints may be related to the forces of rubber elasticity. Alternatively, the kinetics of phase separation slow down because of network formation and/or vitrification. Consequently, metastable phase diagrams can provide information about gelation of polymer I, gelation of polymer II and phase separation of polymer I from polymer II. The proposed metastable phase diagram also serves to describe conditions under which the time order of these three events may be altered.

The model for this study was the polyurethane (PU)–poly(methyl methacrylate) (PMMA) system, with the two networks formed independently by stepwise and chain polymerization mechanisms[3–5]. The monomer (or prepolymer) mixtures for PU and PMMA are denoted in this paper by 'U' and MMA, respectively.

Experimental

The relevant materials for the SIN system are summarized in *Table 1*. The experimental techniques employed are described elsewhere[6]. In brief, an MMA reaction mixture was dissolved in the mixture 'U' in different concentrations. Polymerization kinetics for MMA at each MMA/'U' composition were studied using Fourier transform infra-red *FT*i.r. spectroscopy via *in situ* polymerization, providing conversion–time plots.

The time of phase separation was determined visually by noting the onset of turbidity. A vial inversion method was used to determine the gel point of the first polymer gelling, by noting the time when the reacting liquid stopped flowing. Using the conversion–time plots from parallel *FT*i.r. experiments, the conversions at phase separation and gelation were determined, which were accurate to ±1%, in terms of experimental error in the measurement of time. In this way, a ternary metastable phase diagram was constructed for the system MMA–PMMA–'U'. (The absence of catalyst in the initial mixture 'U' restricts its undesirable polymerization to PU in the experiments involved.) Similarly, a ternary metastable phase diagram was constructed for the system MMA–PMMA–PU, by starting with mixtures of MMA and a linear PU.

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Table 1 SIN materials and recipes used

Compound	Class	Amount	Supplier
Polyurethane			
Poly(oxypropylene) glycol (PPG); $MW = 2000$	Polyether diol	1.0 equiv.	Polysciences
Dicyclohexylmethane-4-4′-diisocyanate ($H_{12}MDI$), Desmodur W	Aliphatic diisocyanate	2.0 equiv.	Miles, Inc.
2-Ethyl-2-(hydroxymethyl)-1,3-propane diol or trimethylolpropane (TMP)	Crosslinker (triol)	1.0 equiv.	Aldrich
2-Butyl-2-ethyl-1,3-propanediol (BEPD)	Chain extender (diol)	1.0 equiv.	Eastman Chemical
Dibutyl tin dilaurate (T12)	Tin catalyst	0.05% (w/w PU)	Aldrich
Poly(methyl methacrylate)			
Methyl methacrylate (MMA)	Monomer	96.5–99.0%	Aldrich
Tetraethylene glycol dimethylacrylate (TEGDM)	Crosslinking monomer	0.5–3.0%	Polysciences
Lauroyl peroxide (LPO)	Initiator	0.5%	Aldrich

Polymerization temperature = 60°C

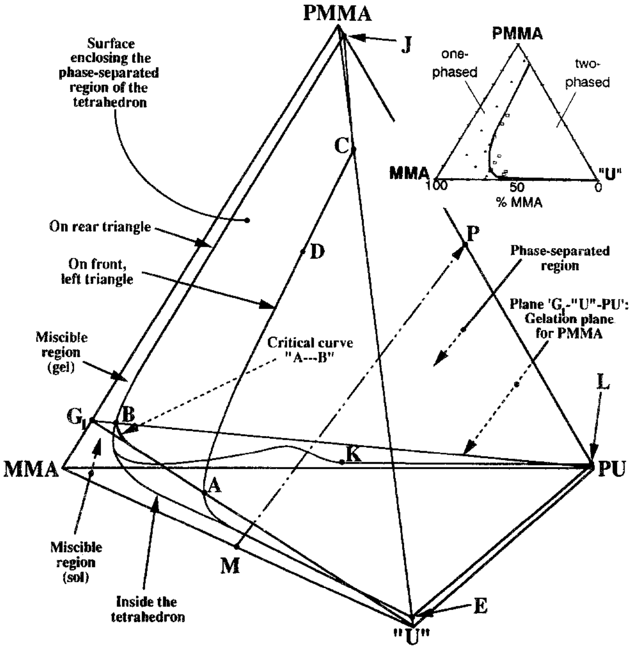

Figure 1 Metastable phase diagram for the four-component system of an SIN: PMMA, PU, MMA and 'U'. Temperature = 60°C. The PMMA gels on and above the plane G_1–'U'–PU. The surface enclosing the phase-separated region in the tetrahedron is marked C–D–A–E–L–K–B–J. Especially note the intersection of the PMMA gelation plane and this surface along 'A–B', a critical curve representing the condition of simultaneous phase separation and PMMA gelation. Inset: The front left face of the tetrahedron, MMA–PMMA–'U', shown with its phase-separation curve as determined experimentally: ▲, miscible (clear) compositions; □, immiscible (turbid) compositions

Dynamic Analyzer (RDA-II) and differential scanning calorimetry on a Mettler DSC-30 were used for modulus and glass transition determination.

Results

Combining the two ternary metastable diagrams described above, a three-dimensional tetrahedron, representing the four-component SIN system MMA–'U'–PMMA–PU, was developed (see *Figure 1*). The four vertices represent the pure components, PMMA, PU, MMA and 'U', and the four triangular faces represent ternary systems.

The phase-separation curve for MMA–PMMA–'U', the front left triangle, is represented by points C–D–A–E. Similarly, the phase-separation curve for the MMA–PMMA–PU system, the rear triangle, is indicated by points J–B–K–L. The entire tetrahedron volume is divided into two regions, one-phased and phase-separated, by a phase-separation surface, indicated by points C–A–D–E–L–K–B–J. The diagram in *Figure 1* is shown with the curves slightly moved from the end points J, L and E to ease visualization, maintaining, however, its overall qualitative features. The inset in *Figure 1* shows the front left face of the tetrahedron with the actual experimentally determined curve, along with data points. The curve in the inset corresponds to curve C–D–A–E in the tetrahedron.

Figure 1 also shows a plane, G_1–'U'–PU, that represents the gelation of PMMA at 8% conversion of MMA, with 0.5% crosslinker (tetraethylene glycol dimethacrylate). A PMMA-containing phase is a sol below this plane and a gel above it. The intersection of this gelation plane with the phase-separation surface forms a curve 'A–B', which is a critical curve in terms of determining the order of events in this SIN system.

A typical initial monomer/prepolymer reaction mixture is represented by a point 'M' (for monomers) lying on the line MMA–'U', depending on the composition of the two components. The resulting fully polymerized SIN may be represented by a similar point, 'P' (for polymers) on the line PMMA–PU. With simultaneous polymerizations for both networks, the system will move along the arrow from point 'M' to point 'P', through the tetrahedron, as the monomers are converted to polymers. This path will intersect the phase-separation

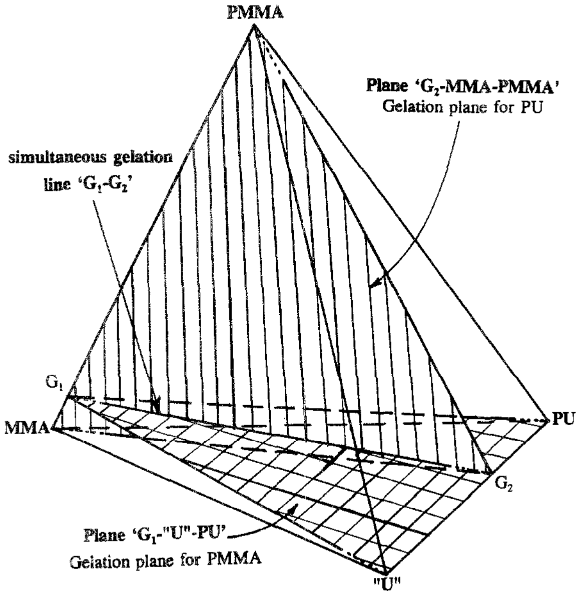

Figure 2 The four-component composition diagram for the same PU–PMMA SIN system as in *Figure 1*, showing the two gelation planes. Plane G$_1$–'U'–PU represents gelation of PMMA at 8% conversion, and plane G$_2$–MMA–PMMA represents that of PU at 67% conversion

surface at some point, beyond which two phases will exist. A reaction path to the left of the critical curve 'A–B' meets the PMMA gelation plane first, followed by the phase-separation surface, whereas a reaction path moving on its right side will undergo phase separation first, followed by the gelation of PMMA. Preliminary MMA polymerizations within the system MMA–PMMA–'U' have indeed resulted in chalk-white samples formed through the latter scheme, and translucent samples formed through the former. This may indicate that gelation of PMMA before phase separation restricts the domain size.

The gelation of PU forms another plane, G$_2$–MMA–PMMA (see *Figure 2*), where the point G$_2$ represents 67% PU conversion in bulk determined by *FT*i.r. experiments. The statistical theory of Flory and Stockmayer[7] suggests gelation at 82% conversion, but the formation of allophanate linkages leads to earlier gelation. The intersection of the two gelation planes forms a critical line G$_1$–G$_2$, representing the simultaneous gelation of PMMA and PU. Simultaneous gelation in SINs is a condition which has been considered to promote dual-phase continuity[8]. It may be noted that PMMA may never gel very close to the points 'U' and PU, because of its extremely dilute state. In fact, its gelation plane may bend slightly upwards in this region in such a way that it meets the lines PMMA–'U' and PMMA-PU at points slightly above points 'U' and PU, respectively. Similar arguments may be applied to the gelation of PU. However, the overall features of *Figures 1* and *2*, i.e. the presence of gelation surfaces, a line of simultaneous gelation and a critical curve 'A–B' should remain unaffected. In fact, the concepts underlying *Figures 1* and *2* are perfectly general, and should work for other systems as well. Most importantly, different polymerization routes may be taken, by first polymerizing one polymer and then the other[9].

Discussion

Such routings can lead to a different order of occurrence of phase separation and the two gelations. Starting from an initial point 'M' on the line MMA–'U' in *Figure 1*, one may choose different paths leading to one of the three important events, i.e. gelation of polymer I, gelation of polymer II, or phase separation of polymer I from polymer II. For example, PU gelation can be achieved first by moving along the bottom face of the tetrahedron, MMA–'U'–PU, by polymerizing the PU alone. The MMA polymerization may be inhibited by using an inhibitor, or controlling temperature or light intensity, until the PU gelation plane is crossed. Similarly, PMMA gelation may be achieved first, provided the composition relative to the position of the critical point 'A' is suitable, by moving along the front left face, MMA–'U'–PMMA. This may be done by polymerizing MMA using photoinitiation at a low temperature, so that the PU formation rate can be kept low enough, until the PMMA gelation plane is crossed. Finally, it is easiest to achieve phase separation first, by 'straight through' polymerization, e.g. along the line M–P. Both PU and PMMA need to be polymerized at comparable rates, the system phase separating before either polymer's gelation under most conditions.

Conclusions

Phase separation and gelation in SINs has been addressed by developing metastable phase diagrams, which allow for representation of phase separation and gelation of two networks. The four-component SIN system, MMA–'U'–PMMA–PU is thus represented as a tetrahedron in three dimensions. This allows visualization of the SIN formation process and provides direction for controlling the specific order of three events (gelation of polymer I, gelation of polymer II and phase separation of polymer I from polymer II).

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