The kinetic peculiarities of interpenetrating polymer network formation

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Using the method of attenuated total internal reflection, infra-red spectroscopy has been used to study the kinetics of formation of the interpenetrating polymer network (IPN) formed between polyurethane and polyesteracrylate. It was found that the curing rates of the different networks are related and an increase in the polymerization rate of oligoesteracrylate leads to changes in the rate of polyurethane formation in IPN. The effects observed are explained in terms of the interdependence of the processes of network formation and microphase separation. The degree of segregation of the components in the IPN depends on the rate of formation of each of the networks.

(Keywords: IPN; phase separation; kinetics; polyurethane; tensile strength)

INTRODUCTION

Interpenetrating polymer networks (IPNs) may be considered as self-organizing systems because their formation occurs under non-equilibrium conditions[1]. The simultaneous processes of reaction and phase separation are typical for IPNs, with the phase separation resulting from the incompatibility of the growing chains. As a result, the reaction conditions and rate of formation of both constituent networks influence the phase morphology of the system and its properties. The kinetics of IPN formation has been studied previously[2–5], however, there are few investigations on the relationship between chemical kinetics and microphase separation in IPNs[6–7]. This paper aims to establish a correlation between reaction kinetics and the properties of the IPN.

EXPERIMENTAL

IPNs based on polyurethane (PU) and oligoesteracrylate [OEA, tri(oxyethylene)-α-ω-dimethacrylate] are produced by simultaneously curing the constituent components. The curing rate of pure PU was determined using the trimethylolpropane-toluyldiisocyanate to polyoxytetramethyleneglycol ($M_w = 1000$) ratio. In all experiments the ratio used was 2:1 g equiv.$^{-1}$. With this ratio of components the infra-red (i.r.) absorption in the region of NCO groups was taken to be 100%. The attenuated total internal reflection (ATIR) method was used on thin film (1.0–1.5 μm) where[8] the OEA polymerization rate was regulated by the initiator concentration. Azobisisobutyronitrile was used as the initiator: series 1, 0.01; series 2, 0.5; series 3, 3.0 mass%. The reaction mixture was poured directly on to the ATIR elements maintained at 80°C. The degree of conversion of the isocyanate groups in the adduct and of the unsaturated bonds in the OEA were followed from the intensities of the i.r. bands at 2270 and 1640 cm^{-1}, respectively[9]. The CH_2 stretching vibration band was chosen as an internal standard. The degree of microphase separation was calculated from relaxation maxima as described elsewhere[10].

RESULTS AND DISCUSSION

Figures 1 and *2* show the extent of conversion with time of PU and OEA in the IPN separately and as a mixture. It can be seen from the slopes that the crosslinking rates of the constituent networks in the IPN are interdepen-

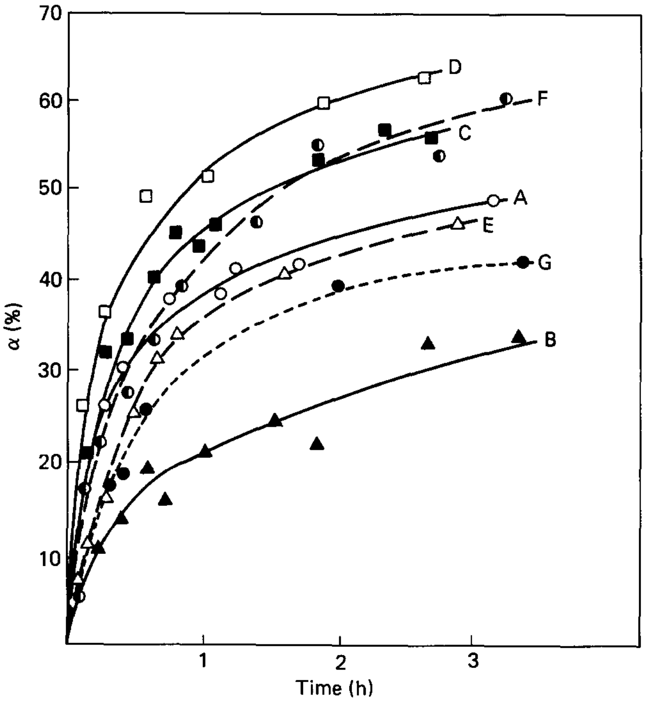

Figure 1 Kinetic curves of curing of pure PU (A) and PU in the IPN with 0.3 (E), 0.5 (B), 2 (C, F, G) and 20 (D) wt% PEA. Series 1, curves A–D; series 2, curves E and F; series 3, curve G

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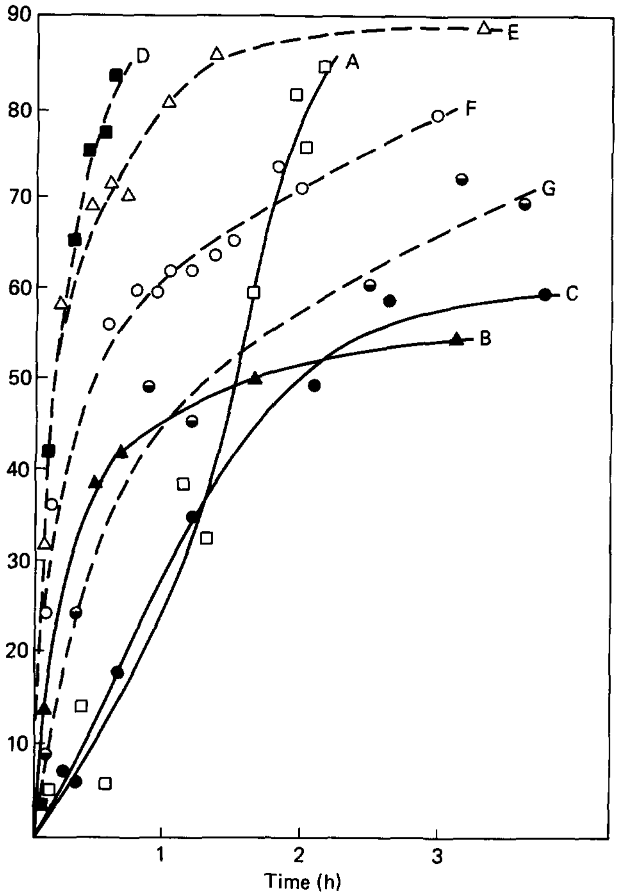

Figure 2 Kinetic curves of polymerization of pure OEA (A, D) and OEA in the IPN with 10 (E), 30 (B, F) and 50 (C, G) wt% PU. Series 1, curves A–C; series 2, curves D–G

dent. We have shown separately that this mutual effect is not connected with the chemical interaction between the networks (no new bands were found in the spectra). It was found that only with high amounts of initiator (>2%) was some retardation of the urethane formation reaction observed.

The influence of the polyesteracrylate (PEA) network on the curing rate of the adduct is more pronounced for experiments in series 1 with a small amount of PEA (*Figure 1*), i.e. with a negligible amount of initiator in the reaction mixture. Therefore, the possible side reactions during the IPN formation can be disregarded.

By differentiating the curves the instantaneous curing rates $\partial\alpha/\partial t$ for PU and PEA were determined. The dependence of $\partial\alpha/\partial t$ on IPN composition at various initiator concentrations and for a definite time interval gives a set of curves characterizing the influence of constituent networks on the curing rate for PU (*Figure 3*) and PEA (*Figure 4*) at various stages of IPN formation.

The urethane formation rate in the IPN, especially at the beginning of the reaction, depends both on PEA concentration and its curing rate (*Figure 3*). In the region of small additions of PEA, the latter diminishes the curing of PU. The effect is more pronounced in the initial reaction stages and depends on the ratio of curing rates of individual networks. More effective inhibition of PU curing was observed in experiments in series 1, where PEA in the IPN was cured with a lower rate than the PU. After 5 min following the beginning of the reaction the PU formation rate in the IPN is 1.5 times slower than that of PU alone. In experiments of series 2, with faster rates, PEA inhibits PU matrix formation less effectively. In series 3 the effect is observed over a wider composition range. The inhibition effects of the initiator seem to contribute to the effects described above.

In the region of intermediate composition of the IPN, OEA accelerates PU curing in the initial stage of the reaction, with the effects being dependent on the OEA crosslinking rate. When a three-dimensional network is well developed the influence of OEA on the PU formation diminishes, the adduct curing rate in IPN becoming close to that for pure PU.

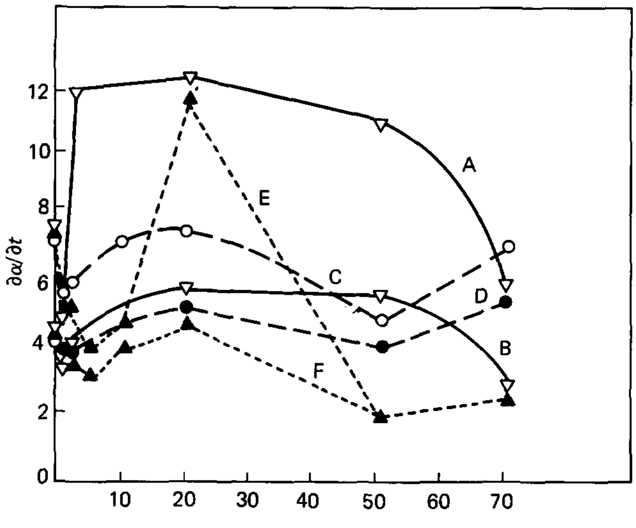

Figure 3 Dependence of PU curing rate on the IPN composition for 5 (A, C, E) and 10 (B, D, F) min after reaction onset. IPN with: 0.01 (A, B); 0.5 (C, D); 3% initiator (E, F)

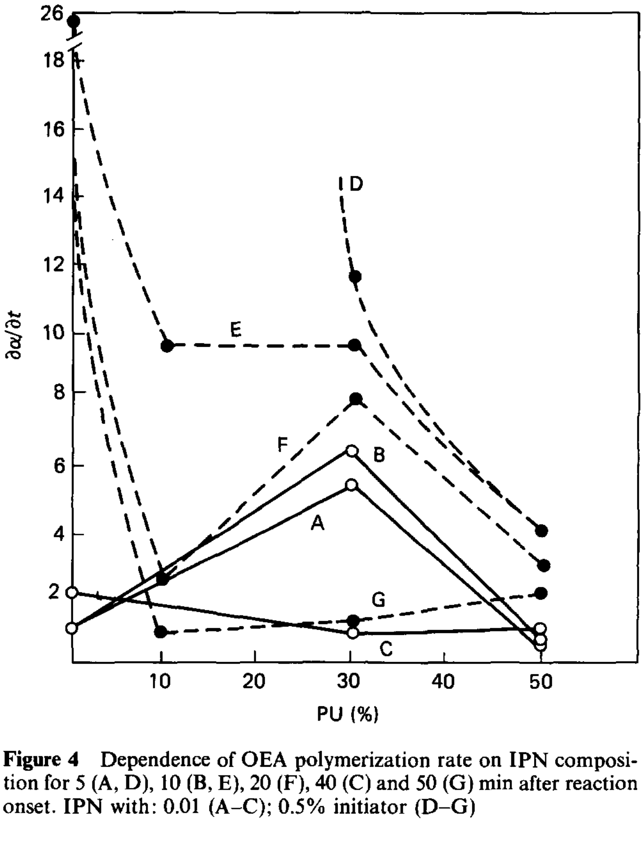

Figure 4 Dependence of OEA polymerization rate on IPN composition for 5 (A, D), 10 (B, E), 20 (F), 40 (C) and 50 (G) min after reaction onset. IPN with: 0.01 (A–C); 0.5% initiator (D–G)

Table 1 The maximum position ($\tilde{\nu}$, cm^{-1}) and half-width ($\Delta\tilde{\nu}_{1/2}$) of C=O stretched vibrations

Sample	PU/OEA (% of initiator)	Time (min)							
		0		7–10		20–30		120–300	
		$\tilde{\nu}$	$\Delta\tilde{\nu}_{1/2}$	$\tilde{\nu}$	$\Delta\tilde{\nu}_{1/2}$	$\tilde{\nu}$	$\Delta\tilde{\nu}_{1/2}$	$\tilde{\nu}$	$\Delta\tilde{\nu}_{1/2}$
1	100/0	1730, 1740	52	1710, 1720, 1740	54	–	–	1719, 1733	52
2	99.7/0.3 (0.5)	–	–	–	–	1739	48	1723, 1732	50
3	99.5/0.5 (0.01)	1725, 1738	44	1729, 1739	48	1713, 1723, 1733	50	1710, 1722, 1734	50
4	98/2 (0.01)	1715, 1720, 1734	45	1720, 1735	45	1715, 1732	49	1717, 1732	49
5	98/2 (0.5)	1730, 1740	46	1730, 1739	45	1737	46	1731	48
6	0/100 (0.01)	1717	23	1717	24	1718	24	1720	29

The PEA formation rate in the IPN in its turn depends not only on the amount of initiator but also on the PU content (*Figure 4*). The PU influence depends strongly on the OEA polymerization rate. In the IPNs of series 1, PU has higher curing rates and facilitates OEA polymerization. At the same time in series 2 the PU curing rate is lower than for OEA and PU inhibits the PEA network formation. In this way the rates of formation of the two networks in the IPNs are interconnected and the change in the reaction rate of one of the networks is reflected in the reaction rate of the other. The degree of this influence and its direction depend on the IPN composition. The same component, depending on its curing rate and volume fraction in the reaction mixture, can accelerate or retard the formation of the second network. The same effects have been observed by us for another IPN[6].

We believe that the fundamental basis for the phenomena described above involves the interdependence of the processes of crosslinking of networks in IPN formation and their microphase separation. The reaction rate of IPN formation strongly influences the onset of phase separation. Using the ATIR method we have shown the presence of intermolecular interactions in IPNs (C=O vibration band) and observed that the introduction of small amounts of OEA into the PU reaction system narrows the C=O vibration band and shifts it to a lower frequency (*Table 1*). At low concentration the addition may alter the spectra only if it is uniformly distributed. This means that in the initial reaction mixture the contacts between components forming the two networks are preferred. As a result, OEA retards the PU crosslinking in the initial stages of reaction. In the course of curing the chemical composition of the system and the intermolecular interactions in it change continuously (*Table 1*). The thermodynamic incompatibility of growing networks arises at a definite degree of conversion, initiating the microphase separation. After its beginning the influence of the additive on the PU matrix network formation should become weaker. In fact the adduct curing rate in IPN approaches the value of the curing rate of pure PU. In due course in the separated PU microphase, microregions of hard blocks are formed. This is in agreement[11,12] with the appearance of bands of self-associated urethane groups at 1710–1720 cm^{-1}. Correspondingly for sample 3, in which initially the reaction rate of PU formation is lower than that of the pure PU (*Figure 3*) the bands of self-associated groups in the i.r. spectra appear later. The coincidence of carbonyl absorption parameters (position and half-width) in the initial spectra of PU and IPN with 2% OEA and 0.5% initiator (sample 5) and the presence of bands of self-associated groups show that with increasing OEA concentration the time of the microphase separation onset diminishes. The process of microphase separation proceeds, during the time needed for the spectrum to be measured. The decrease of this time with increasing content of the second network has been observed for IPNs using PU and the styrene–divinylbenzene copolymer[13]. The simultaneous processes of chemical reaction and microphase separation lead to a continuous change in the phase volumes ratio and their composition. This explains why the influence of the PEA network on urethane formation depends on the amount of initiator. The microregions of the PEA network evolved in the initial reaction stage distribute uniformly in the PU matrix playing the role of 'filler'. The continuous PEA network in the PU matrix does not form at a PEA content of ~2%. For samples in series 1 the PEA network markedly accelerates the urethane formation reaction in the initial stages. This may be due to an increase in incompatibility which leads to the local increase in concentration of components for PU formation and to an increasing reaction rate. At the same time the PEA network may act as a filler which adsorbs components of the PU network and thus accelerates the urethane formation.

With increasing curing rate of PEA there is a sharp increase in viscosity, which hinders the component diffusing and microphase separation. Even in the fully cured system the level of microphase separation is low: the urethane group self-association bands in the i.r. spectra are absent (initiator concentration 0.5%, *Table 1*, sample 5). The same conclusion follows from the temperature dependence of the mechanical loss tangent for PU and PEA (*Figure 5*, curves C, D) and for the two IPNs with the same composition (10% PEA) but with various rates of OEA polymerization (0.5% initiator, curve B and 3% initiator, curve A, *Figure 5*). Two maxima are observed for tan δ in the temperature region close to the corresponding temperature for each component. The shifts in temperature of the mechanical loss maximum which can be detected are the result of incomplete phase separation and of the dependence of the degree of phase separation on the rate of network formation. For the IPN where the PEA network is formed earlier (*Figure 4*, curve G) a merging of the mechanical loss maxima is observed. This testifies that the degree of microphase separation diminishes. The

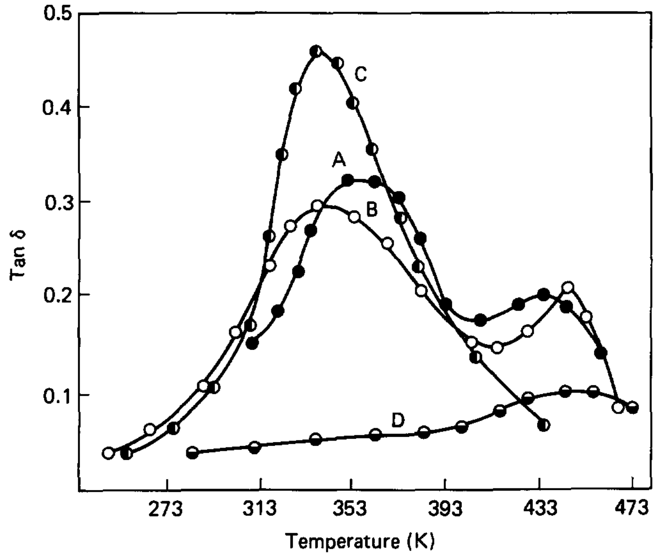

Figure 5 Temperature dependence of tangent of mechanical loss for PU (C), PEA (D), IPN with 10% PEA (0.5% initiator) (B) and IPN with 10% PEA (3% initiator) (A)

segregation degree, which is a quantitative measure of microphase separation, calculated according to reference 10, is equal to 0.75 for the IPN when the PEA network is formed rapidly and 0.85 for the IPN with a low polymerization rate of OEA. This decrease in the rate of formation of one of the networks (in this case PEA) leads to increasing microphase separation in the IPN.

In this way the structure of the IPN is determined by superposition of two processes. The processes are the formation of each network and microphase separation due to the increase in thermodynamic incompatibility. The properties of the IPN are dependent on the ratio of the reaction rate for both networks.

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