

SYNTHESIS AND PROPERTIES OF POLYURETHANE ACRYLATE/EPOXY RESIN INTERPENETRATING POLYMER NETWORKS

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ABSTRACT

In this paper, a series of interpenetrating polymer networks (IPNs) based on polyurethane acrylate and epoxy resin was prepared by simultaneous photoinitiating by both free-radical and cationic polymerization. The effects of the polyurethane acrylate prepolymer's molecular weight, various components ratio and polymerization methods on IPN's dynamic mechanical and mechanical properties were investigated.

INTRODUCTION

In the literature^[1], a number of methods have been reported for the preparation of IPNs, such as sequential IPNs. The first synthesized crosslinked polymer I is swollen with a second monomer II containing its own crosslinker and initiator, and polymerized in situ. Besides simultaneous IPNs synthesis refers to mixing of monomers or prepolymers, crosslinkers, etc., and both components are then simultaneously polymerized by independent, noninterfering reactions. Frisch et al.^[2-8] have reported on the preparation of polyurethane/epoxy resin IPNs by heating curing. However, the study on preparing IPNs by ultraviolet initiating simultaneous polymerization has not been reported.

In this paper, polyurethane acrylate/epoxy resin IPNs were prepared by ultraviolet light simultaneous initiating both free-radical and cationic polymerization. Their dynamic mechanical and mechanical properties were studied.

EXPERIMENTAL

Materials

Toluene diisocyanate (TDI): reagent grade, purified by vacuum distillation.

Polyethylene glycol (PEG): reagent grade, was dried at 60°C for 24 hours under vacuum.

Epoxy resin (EP): diglycidylether of bisphenol A with an epoxy number 5.1meq/g

Hydroxypropyl acrylate (HPA), potassium iodate, dibutyltin dilaurate (T-12), benzoin n-butyl ether and other materials were used without any further purification.

Synthesis

Polyurethane acrylate (PU) prepolymer: One equivalent of HPA was slowly added into a flask containing 2 equivalent of TDI. Hydroquinone and phenothiazine were added as inhibitor. After this reaction was completed, one equivalent of dehydrated polyol and several drops T-12 as catalyst were slowly added. It took additional 2 hours or more to complete the reaction as monitored by IR. The characteristic NCO absorption of TDI at 2270 cm^{-1} disappeared. The reaction temperature was not allowed to over 70°C. The following PU prepolymers were synthesized:

PU-200, PU-400, PU-600, PU-800, PU-2000 (The numerical numbers indicate the molecular weight of PEG segment, respectively.)

Cationic photoinitiator: Diphenyliodonium tetrafluoroborate ($\text{Ar}_2\text{I}^+\text{BF}_4^-$) was synthesized according to the known method in the literature. Melt point is 136—136.5°C [lit. 136°C]^[9].

Samples Preparation

PU Networks: About 2wt% benzoin *n*-butyl ether was added into PU prepolymers as photoinitiator, stirring, and the removing bubble by vacuum. The liquid prepolymers were poured into teflon molds. The samples were cured by ultraviolet light from a GGU-500W high pressure mercury lamp.

EP Networks: EP containing dissolved 2wt% diphenyliodonium tetrafluoroborate as photoinitiator was polymerized by exposure to ultraviolet light from the same lamp as above.

PU/EP IPNs: The mixture of PU, EP, and 2wt% of two kinds of photoinitiator was dissolved into a portion of acetone to ensure homogeneous mixing and solvent and bubble were removed by vacuum. Then followed the same operation as above.

In order to cure the samples completely, it was heated for a short time or at room temperature for fifteen days, and then measured their properties.

Characterization Methods

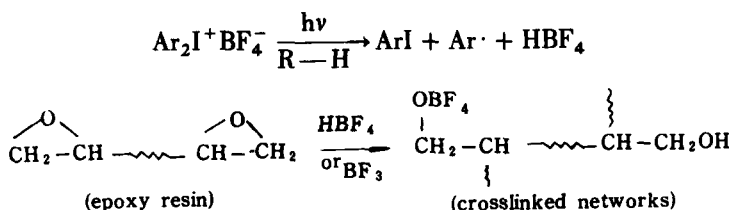
Dynamic Mechanical Measurements: Dynamic mechanical data were collected at 3.3Hz using a Japan N-VES viscoelastometer with a heating rate of 2°C/min. Samples of about 40 × 4.5 × 1.0mm were tested.

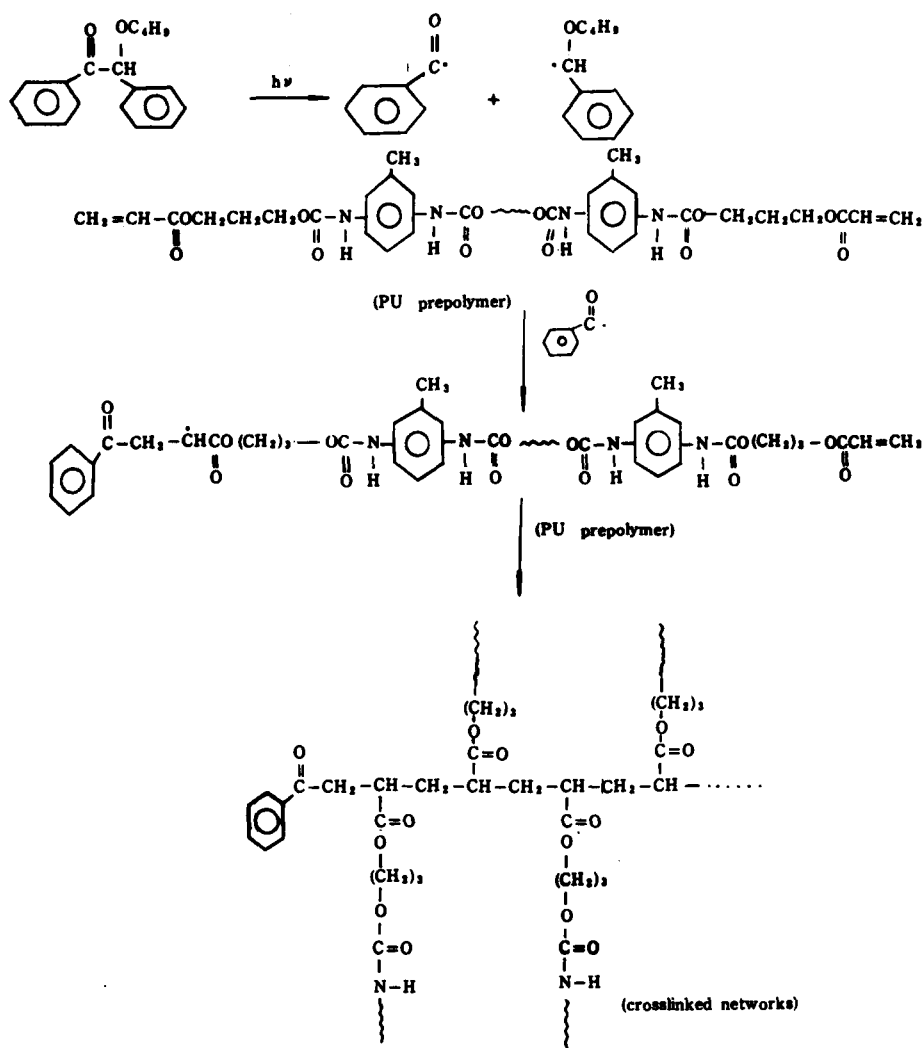
Stress-Strain Measurements: Stress-strain measurements at room temperature were made by using 1122 Instron with a crosshead speed of 10mm/min. Dumbbell shaped film samples with a gauge length of 30mm were stamped out with an ASTM 412 die.

RESULTS AND DISCUSSION

It is well known that some factors such as compatibility of the polymers, crosslink density of the networks, relative curing rate of two component prepolymers, affect the morphology of IPNs. The morphology strongly influences most of the physical and mechanical behavior of the IPNs. When other conditions are fixed, the relative rate of phase separation and two networks entanglement affects the morphology of IPN's. If the chains were crosslinked before the phase separated, the crosslink might inhibit the phase separation to some extent. So various morphology of IPNs may be obtained by controlling the relative curing rate of two component polymers.

IPNs are novel blends of crosslinked polymers containing essentially no covalent bonds, or grafts, between them. Both components are simultaneously polymerized by their own mechanism reaction. In this paper, we have studied on the PU/EP system, the former crosslinked according to free-radical polymerization under exposure to ultraviolet light, and the latter crosslinked by cationic polymerization in the presence of diphenyliodonium tetrafluoroborate under exposure to ultraviolet light.





When the homogenous mixture of two prepolymers and two kinds of photoinitiator was exposed to ultraviolet light, they crosslinked by different mechanism, and no or little interference involved, as shown from IR spectra, the positions of all the bands in IPNs were the same as the corresponding components. This indicated that within the limitations of the IR technique, there is no reaction between the consisted polymers during the curing. All the samples only swell, but do not dissolve in acetone.

The dynamic mechanical storage modulus(E') and loss factor ($\tan \delta$) curve for PU networks from various molecular weight polyol are shown in Figure 1. The loss factor curve shows that as the polyol molecular weight decreasing, the two transition peaks of PU networks glass transition become one broader transition peak, then one sharp peak. And the position of the transition peak shifts to higher temperature. It is suggested that crosslink density increases with shorter (lower molecular weight) polyol chains, and the compatibility of soft-segment and rigid-segment increases. Increasing crosslink density also results in decreasing the motion of segment, and thus the T_g rises.

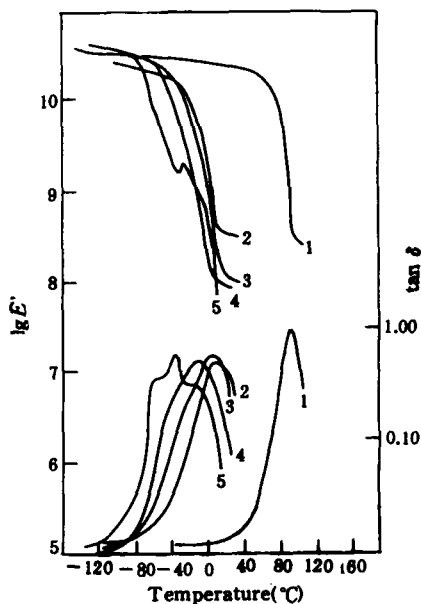


Fig. 1 Dynamic mechanical storage modulus(E') and loss factor ($\tan \delta$) curves for PU networks.
1. PU-200; 2. PU-400; 3. PU-600; 4. PU-800; 5. PU-2000

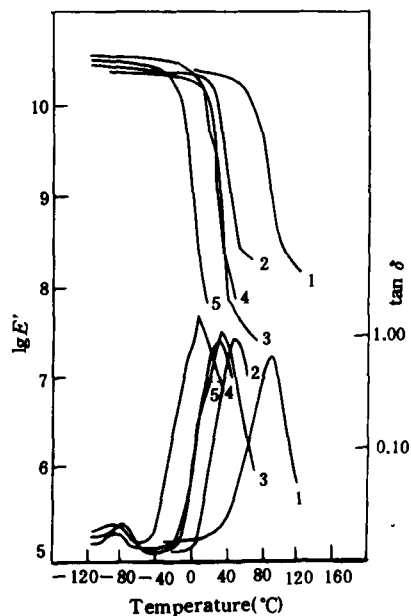


Fig. 2 Dynamic mechanical storage modulus(E') and loss factor ($\tan \delta$) for the IPNs consist of various molecular weight PU and EP (weight ratio = 1:1)
1. PU-200/EP; 2. PU-400/EP; 3. PU-600/EP;
4. PU-800/EP; 5. PU-2000/EP

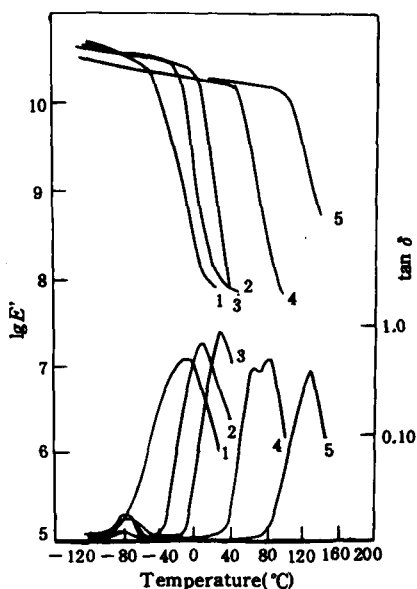


Fig. 3 Dynamic mechanical storage modulus(E') and loss factor ($\tan \delta$) for various proportion of PU-800/EP IPN's
1. 100%PU-800; 2. 80%PU-800/20%EP; 3. 50%PU-800/50%EP; 4. 20%PU-800/80%EP; 5. 100%EP

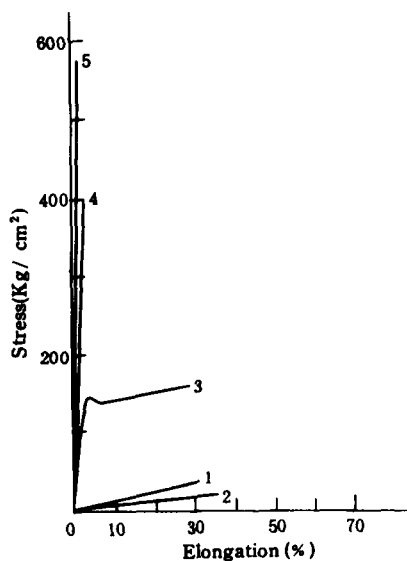


Fig. 4 Stress-strain curves for IPNs
1. 100%PU; 2. 80%PU-800/20%EP; 3. 50%PU-800/50%EP; 4. 20%PU-800/80%EP; 5. 100%EP

The dynamic mechanical storage modulus and the loss factor for the IPNs consisting of various molecular weight PU and EP (weight ratio = 1 : 1) are shown in Figure 2. It shows that the decreasing of PU molecular weight results in the IPN's transition peaks to be narrowing and sharpening, the IPN's T_g also shifts to higher temperature. As the crosslink density of PU increases the extent of interpenetration of two component networks enhances, and the compatibility of two component networks also increases. It may be due to that the rate of free-radical polymerization is faster than the cationic polymerization's. The crosslink density of the first formed network controls the domain size of the second network.

Dynamic mechanical storage modulus and loss factor for various proportion of PU-800/EP IPNs are shown in Figure 3. When PU-800/EP weight ratio equals to one, the IPN's transition peak is the narrowest and sharpest. Since the shift and broadening of the T_g 's of component polymers can reflect the degree of molecular mixing, it suggests that the degree of the networks mixing between two components is the greatest.

Stress-strain curves for IPNs are shown in Figure 4. When the PU-800/EP weight ratio is one, a yield point appears, which results from a typical toughness system. Hence, it indicates that as the extent of two component networks interpenetration increases, the toughness of this system increases significantly. The minimum in tensile strength occurs at 80% PU. This is in agreement with the results obtained previously in the literature^[4]. The minimum is most likely due to initial weakening of the PU structure due to the disruption of hydrogen bonding at small values of X_c' .

From Table 1, it can be seen that the θ value of this system (PU-800/EP = 1 : 1) is relatively great. According to $\theta = (F_x/F_m - 1)X_c'^{[10]}$ (X_c' is a measure of the extra crosslink density due to interpenetration.), it has been reported that the greater the θ value, the more entanglement of the

Table 1 Glass transition temperature

Composition	T_g K(e)	T_g K(c)	T_g K(a)	θ
100%PU-800	265	—	—	
80%PU-800/20%EP	279	284	292	0.0466
60%PU-800/40%EP	296	306	319	0.0777
50%PU-800/50%EP	298	319	332	0.1141
40%PU-800/60%EP	330	332	346	0.0485
20%PU-800/80%EP	355	363	373	0.0507
100%EP	400.5	—	—	
100%PU-200	364	—	—	
100%PU-400	283	—	—	
100%PU-600	280.5	—	—	
100%PU-2000	239	—	—	
100%PU-2160	222	—	—	

T_g (e) — experimental

T_g (c) — calculate : $1/T_g(c) = W_1/T_{g1} + W_2/T_{g2}$

T_g (a) — average: $T_g(a) = W_1 T_{g1} + W_2 T_{g2}$

$(T_g(e) - T_g(a)) / T_g(a) = -\theta / (1 - \theta)$

two component polymers. This is consistent with the system's dynamic mechanical and mechanical properties.

Dynamic mechanical storage modulus and loss factor for IPNs by different preparing methods are shown in Figure 5. The glass transition peak of IPNs prepared by simultaneously photoinitiating polymerization is narrower and sharper [curve 1.] than by sequential polymerization, which the crosslinking of PU by ultraviolet light first, and then the crosslinking of EP containing 5wt% 2-ethyl-4-methylimidazole as crosslinker by heating give a broader transition peak with a shoulder [curve 2.], as a result of phase separation. It explains that the extent of IPN's interpenetration prepared by simultaneously photoinitiating polymerization is greater than the sequential polymerization. This is in consequence of that the rate of simultaneously photoinitiating polymerization is faster than the sequential polymerization. Therefore, the phase separation was restricted effectively by rapidly forming IPN's chains entanglement, hence kinetically inhibited by permanent interlocking of entangled chains in simultaneously photoinitiating polymerization. In sequential polymerization, the solubility of the PU prepolymer decreases with photopolymerizing in EP, so some crosslinked PU networks will be separated out and leads to phase separation. It may be considered that the effect of permanent interlocking of entangled chains in simultaneous photoinitiating polymerization is more effective kinetically than that in sequential polymerization.

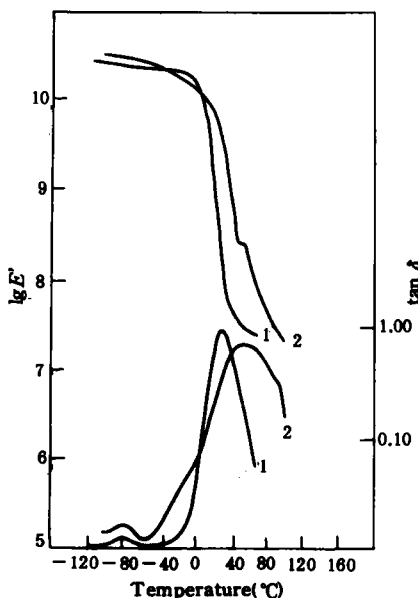


Fig. 5 1. Simultaneous photopolymerization 50%PU-600/50%EP IPN

2. Sequential 50%PU-600/50%EP IPN

(first crosslinking PU by UV light, then crosslinking EP by heat)

Keywords:

Interpenetrating polymer network; UV curing; Photopolymerization; Polyurethane; Epoxy resin

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