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Interpenetrating polymer networks based on polyurethane and polysiloxane

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Abstract

A series of interpenetrating polymer networks (IPNs), based on a polyurethane (PU) and polydimethylsiloxane, has been synthesized and characterized by means of DSC, TEM, TGA, ^{1}H-NMR and IR spectroscopies, and other techniques. The homo-networks have been characterized by swelling in *n*-hexane and chloroform. The IPNs are obtained by combination of a PU based of the castor oil and 2,4-toluene diisocyanate (TDI) with different amounts of polydimethylsiloxane-α,ω-diol (PDMS). These materials have interesting individual physical properties, but some IPNs exhibited superior properties than either of the separate networks. For interesting results, it was used as compatibilizer the polydimethylsiloxane graft polyalkylene oxide. All the IPNs exhibited phase separation and maximum extent at the point of phase inversion.

Keywords: Interpenetrating polymer networks (IPNs); Polyurethane; Polysiloxane; Equilibrium swelling

1. Introduction

Interpenetrating polymer networks (IPNs) are a combination of two or more network polymers synthesized in juxtaposition [1]. A better definition is offered by Kim [2]: an IPN is a mixture of two or more cross-linked polymers with a physically interlocked network structure between the component polymers.

Some publications [3,4] describe polyurethane (PU)–polysiloxane blends that lead to the formation of IPNs. Klempner et al. [3] prepared partial topologically interpenetrating networks from PU-urea and polysiloxanes. The networks have been formed by combining equal weights of the two polymers as aqueous emulsions together with their cross-linking agents and stabilizers. The homogenous mixtures were cast into films. The properties of the resulting materials were not outstanding.

Schurb and Evans [4] prepared IPNs from various diisocyanate prepolymers and an amine—modified polydimethylsiloxane by using a phenol-formaldehyde resin as a cross-linking agent. The reaction was performed in a common solvent. Afterwards the solvent was evaporated and the substrate was heated to effect the cure.

Arkles [5] describe a process by which a blend of polysiloxane and a PU was converted into a semi-IPN during processing. The polysiloxane network was formed by a platinum catalyzed vinyl addition.

The morphology and properties of IPNs depend upon the degree of phase morphology, which is related principally to the miscibility of the polymers [6,7]. The idea is to effect a molecular interpenetration of the networks; in practice, most IPNs form immiscible compositions, usually phase separating, during some stage of the synthesis.

Polymer industry has been challenged to produce new polymeric materials with improved properties by blending different polymers. However, mainly due to unfavourable entropy of mixing most polymers are thermodynamically immiscible with each other. IPNs synthesized to date exhibit varying degrees of phase

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separation depending principally on the miscibility of the polymers [8]. One way of improving the miscibility of two polymers is to use compatibilizers, which are usually block or graft copolymers, consisting of segments that are preferentially miscible with the polymers to be blended. Utilizing compatibilizer agents that promote chemical or physical interactions between the phases can control morphology of IPNs.

2. Experimental

2.1. Materials

- castor oil, [triglyceride of ricinoleic acid (C_{OH} = 140 mgKOH/g, OH = 2.5/mol of castor oil)], local market;
- 2,4-toluene diisocyanate (TDI), 98%, FW 174.16, mp 20–22°, bp 120° /10 mmHg, n_D^{20} 1.5680, d 1.214 g/cm^3, Aldrich;
- glycerol, 99.5%, FW 92.09, mp 20°, bp 192°/20 mmHg, n_D^{20} 1.4740, d 1.261 g/cm^3, Aldrich;
- polydimethylsiloxane-*g*-polyalkylene oxide synthesized according to [9], with d 1.07 g/cm^3, η^{25} 487 cSt and having the composition: polydimethylsiloxane-α,ω-diol (PDMS) 12.34%, PPO 40%, PEO 44%, and acetoxy (Ac) 3.66%;
- PDMS, with Mn = 50,000 was synthesized by ring-opening polymerization of octamethylcyclotetrasilane in presence of cation-exchanger (a styrene-divinylbenzene copolymers with sulphonic groups) [10];
- methyltriacetoxysilane, $(CH_3CO)_3SiCH_3$, (MTAS), was synthesized in our laboratory, according to classical methods for acetoxylation (bp 87–88 °C/3 mmHg, d 1.175 g/cm^3, n_D^{20} 1.4083).

2.2. Prepolymers synthesis

The prepolymer urethane (PPU) was prepared from castor oil and 2,4-TDI, in order to maintain an NCO/OH ratio of 3.5 (leading to an isocyanate-terminated prepolymer). The reaction was carried out at 60 °C for 1 h under stirring and a stream of dry nitrogen, and the prepolymer isolated was a thick liquid. The cross-linking agent for the PPU was glycerol.

The prepolymer siloxane (PDMS) was synthesized by ring-opening polymerization of octamethylcyclotetrasilane in presence of cation-exchanger (styrene-divinylbenzene copolymers with sulphonic groups).

2.3. Interpenetrating polymer networks synthesis

The polyurethane (PU) network was prepared from 2,4-TDI, castor oil and glycerol as cross-linked agent. The polysiloxane (PS) network was synthesized from a α,ω-dihydroxypolydimethylsiloxane, which was cross-linked with MTAS.

In the preparation of the IPNs, stoichiometric quantities of both prepolymers and the cross-linking agents in all cases, and 1% compatibilizing agent based on PDMS graft polyalkylene oxide were used.

Once first phase obtained a PPU based on castor oil and 2,4-TDI. It has dried under vacuum and temperature (120 °C), 200 g (0.2 mol) castor oil for 3 h. When the temperature decreased to 60 °C, was introduced under stirring, 160 g (0.9 mol) of 2,4-TDI (NCO/OH ratio ≅3.5). The prepolymer was maintained under stirring for 1 h.

The PPU together with the compatibilizing agent was dissolved in THF, in conformity with amounts shown in Table 1. After dissolving, THF was evaporated, and the mixture was dried under vacuum and 60 °C, for 1–2 h. Table 1 shows the amounts needed for obtaining these IPNs.

In the second step it was obtained IPNs varying the amount of PDMS from the final product. The prepolymer obtained in first step was mixed with PDMS and MTAS at 80 °C for 1 h. After that cross-linking agent for PU was added, in conformity with Table 1. The product was dried under vacuum, thereupon it was cast as a film. By this means we obtained five IPNs that were codified PUS10, PUS20, PUS40, PUS60 and PUS80. PU and respectively PS homo-network were marked PU and respectively PS.

2.4. Characterization

IPNs has been characterized by thermogravimetric analysis, TGA curves were recorded on an instrument (TGA 2950 Du Pont, USA) at temperatures between 20

Table 1
Interpenetrating networks based on PU–polysiloxane

IPNs composition	PUS10	PUS20	PUS40	PUS60	PUS80
Urethane prepolymer (g)	45	40	30	20	10
Compatibilizer (g)	0.45	0.4	0.3	0.2	0.1
Solvent (THF) (ml)	25	25	25	25	25
Glycerol (ml)	2	1.77	1.33	0.88	0.44
PDMS (g)	5	10	20	30	40
Methyltriacetoxysilane (g)	0.5	1	2	4	5

and 600 °C. The heating rate was 12 °C/min in nitrogen and sample size was 50 mg.

Differential scanning calorimetry (DSC) determinations were performed by a Mettler DSC 12E (T_{start}: +20 °C, T_{end}: +400 °C, heating rate: 10 °C/min, range: 100 μV).

Transmission electronic microscopy (TEM) was done on a TESLA BS513A apparatus type, at a tension $U = 80$ kV. Thin films suitable for electron microscopy were cast onto glycerin from 1% dimethylformamide-dioxane solutions. After slow evaporation of the solvent, the films were placed on grids with inert carbon supports and dried under vacuum at 10^{-4} Torr for several days.

The infrared (IR) spectra were recorded on a Specord M80 Carl Zeiss Jena spectrometer using the KBr pellet technique. Films for study were dried under vacuum to remove the residual solvent.

^{1}H-NMR spectroscopy was utilized and the samples were analyzed in DMSO using a C 80-HL type high resolution NMR instrument, at room temperature using tetramethylsilane as an internal standard.

3. Results and discussion

3.1. Equilibrium swelling

The solubility parameter of polydimethylsiloxane homo-network was determined by swelling in *n*-hexane. Equilibrium swelling ratio was determined using conventional gravimetric method as follows.

$$\text{Swelling ratio} = (W_s - W_d)/W_d,$$

where W_s is the weight of the sample swollen by solvent and W_d the weight of the dried sample. We determined the swelling coefficient, Q. The results are presented in Fig. 1. The maximum in the Q–δ plot occurs at about 14.7×10^3 $(J/m^3)^{1/2}$, which is taken [11] as the solubility parameter of the PDMS network. This value is close to 14.9×10^3 $(J/m^3)^{1/2}$ which is widely used in the literature [12] as the solubility parameter of PDMS. The solubility parameter of the PU network determined in chloroform was 19.3×10^3 $(J/m^3)^{1/2}$ and this result is presented in the same figure.

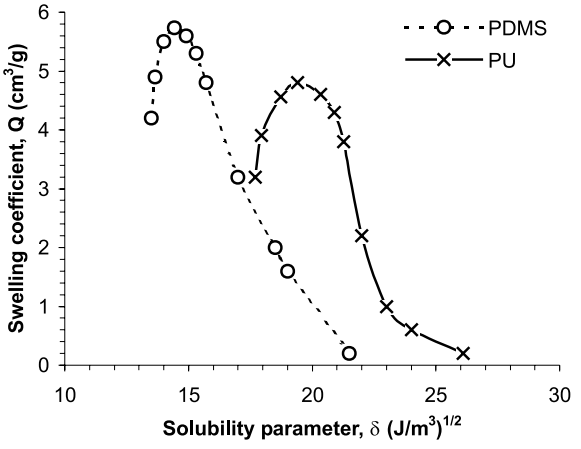

Fig. 1. Swelling coefficient versus solubility parameter for the PDMS and PU homo-networks in *n*-hexane and, respectively, chloroform.

3.2. Sol/gel ratios

In Figs. 2 and 3 are presented the IR and ^{1}H-NMR spectra for the PPU and PU extract in dimethylformamide (DMF), for PUS10, the IPN with the largest amount of PU.

The soluble fractions of the IPNs were effectuated in DMF and toluene and the results are shown in Table 2. The sol/gel ratios obtained for these IPNs compare well with the literature value of upto 7% [13]. The low ratios indicate that the polymer chains have been well incorporated in the network structure.

3.3. Thermal analysis

The IPNs films have analyzed by DSC and TGA.

In Fig. 4 are present thermograms DSC for PUS10, PUS20, PUS40, PUS60, PUS80 and PU.

Fig. 4 illustrates the transitions in IPNs based on PU and polydimethylsiloxane. They show an endothermic peak at temperatures around 300 °C, like the control sample (PU), these temperatures corresponding to the PU structure from the networks. All IPNs show two T_g; the first around 60 °C and the second around 200 °C, which represent the T_g for PU and, respectively, polydimethylsiloxane.

The thermal behaviour of the IPNs was assessed in terms of percent loss in weight at different temperatures. The results are reported in Table 3. It is evident that all the IPNs are stable up to 200 °C, lose weight rapidly around 350–450 °C, and decompose completely beyond 550 °C.

It can be observed from our study of IPNs based on PU and PDMS that the IPNs are superior in thermal stability. Increasing of the amount of polysiloxane into IPNs, produces increasing of the thermal stability. All products decompose in a single step.

The reaction order for all IPN thermal decompositions are close to unity. This suggests that some diffusion processes might accompany the decomposition reactions.

The dependence of the activation energy (Reich and Levi methods [14]) versus conversion degree is presented in Fig. 5.

In Fig. 5 we can remark that the energy of activation decreases until a conversion $\alpha = 0.2$, after that it increases till $\alpha = 0.7$. For $\alpha > 0.7$ the energy of activation decreases again.

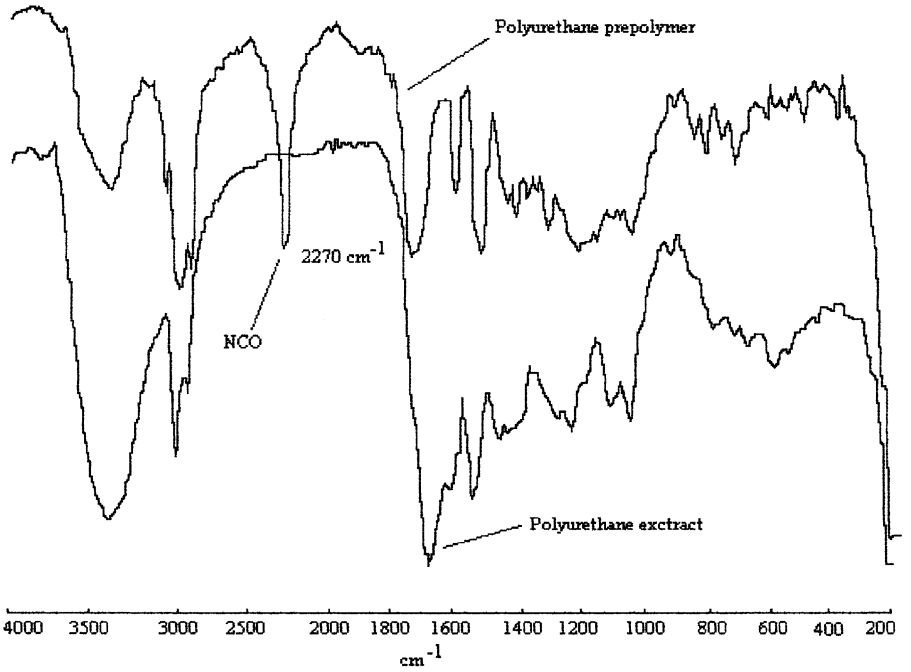

Fig. 2. IR spectra for a PU extract (PUS10) and the polyurethane prepolymer in DMF.

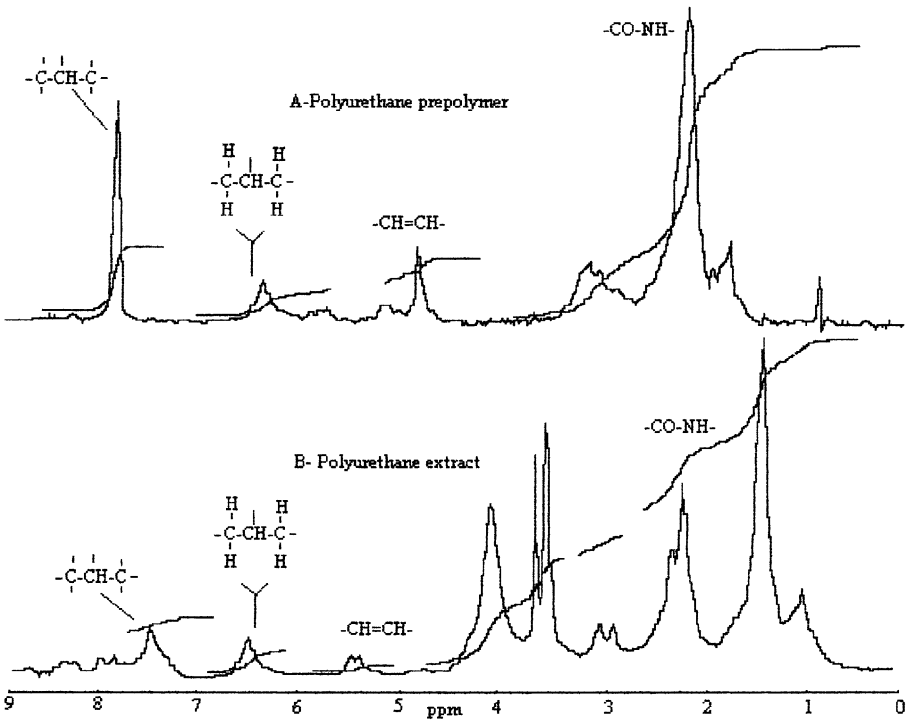

Fig. 3. ^{1}H-NMR spectra for a PU extract (PUS10) and the polyurethane prepolymer.

Table 2
The sol/gel ratios of PUS–IPNs

Code	PU % (w/w)	PS % (w/w)	Sol/gel ratio in DMF (wt.%)	Sol/gel ratio in toluene (wt.%)
PS	0	100	–	6.1
PUS80	20	80	1.8	4.9
PUS60	40	60	2.6	3.8
PUS40	60	40	3.0	2.7
PUS20	80	20	3.3	3.4
PUS10	90	10	4.3	3.1
PU	100	0	5.2	–

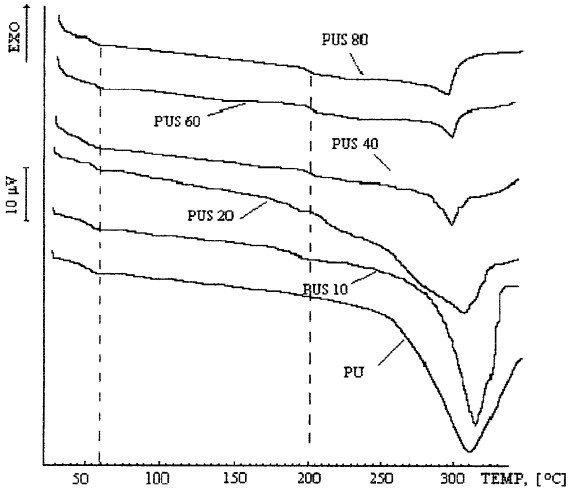

Fig. 4. DSC thermograms for PUS10, PUS20, PUS40, PUS60, PUS80 and PU.

For $\alpha < 0.2$ there appears an important depression in activation energy values versus conversion. This suggests that at the beginning, the reaction has an autocatalytic behaviour. In connection with this, one should note that traces of oxygen in the polymer act as a catalyst for the decomposition process (the oxygen is the initiator of the thermal or thermoxidative reactions).

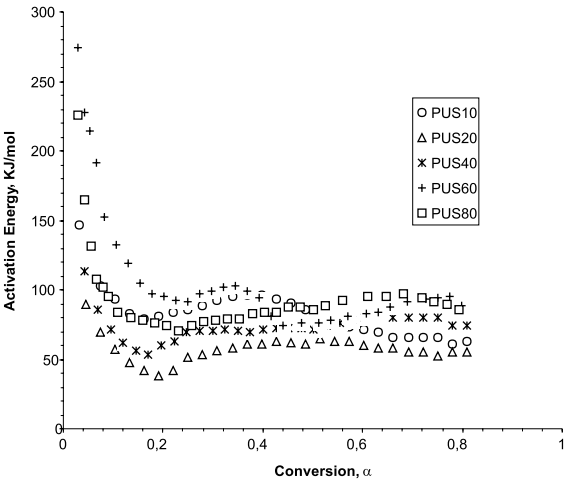

Fig. 5. Activation energy versus conversion for PUS10, PUS20, PUS40, PUS60 and PUS80.

Table 4 presents the overall kinetics parameters for thermoxidative decomposition of PUS10, PUS20, PUS40, PUS60 and PUS80.

We can observe that the IPNs based on PU and polydimethylsiloxane present temperatures corresponding to the maximum rate of weight loss IPNs up to 500 °C for PUS40...PUS80. The influence of the amount of polydimethylsiloxane in the IPNs is the cause of the increase of the thermal stability.

The concordance of the overall values of the kinetic parameters obtained by both, differential and integral methods [14], makes possible an evaluation of the decomposition behaviour of these products.

3.4. Transmission electron microscopy

Fig. 6 shows the PUS10, PUS20, PUS40, PUS60, PUS80 samples that has been studied by TEM.

Some authors describe IPNs, which exhibit varying degrees of phase separation depending principally on the miscibility of the polymers [8].

Table 3
Thermograms of PUS10, PUS20, PUS40, PUS60 and PUS80

Sample code	Reaction order[a]	wt.% loss at temperature (°C)								Energy of activation[a] (kJ/mol)
		200	250	300	350	400	450	500	550	
PUS10	1.1	2	2.5	12.5	35	50	62.5	70	85	43.5
PUS20	1.0	2	4	12.5	32	48	55.5	65	80	45.1
PUS40	1.1	2	3.5	15	30	45	55	65	85	61.1
PUS60	1.2	1	2	3	16	30	52	72	80	57.4
PUS80	0.9	1	1	3	8	10	42	66	78	55.3

[a] Calculated through Reich–Levi method [14].

Table 4
Overall kinetic parameters for thermoxidative decomposition of PUS10, PUS20, PUS40, PUS60 and PUS80

Sample	E_{CR} (kJ/mol)	$\ln A_{CR}$	n_{CR}	E_{LR} (kJ/mol)	T_m (°C) DTG	T_{iso} (°C)	T_i (°C)	T_f (°C)	w_{final} (%)
PUS10	43.5	7.8	1.1	89.7	370	305	200	500	85
PUS20	45.0	11.2	1.0	63.2	390	388	220	500	82
PUS40	61.1	11.6	1.1	84.1	450	418	270	580	84
PUS60	57.4	9.6	1.2	74.1	450	412	270	585	85
PUS80	55.3	7.8	0.9	73.2	450	505	275	590	82

E—overall activation energy evaluated by various methods denoted by subscript; A—pre-exponential factor; n—reaction order; T_i—initial temperature; T_m—temperature corresponding to the maximum rate of weight loss; T_f—final temperature; T_{iso}—isokinetic temperature; w_{final}—final weight loss.

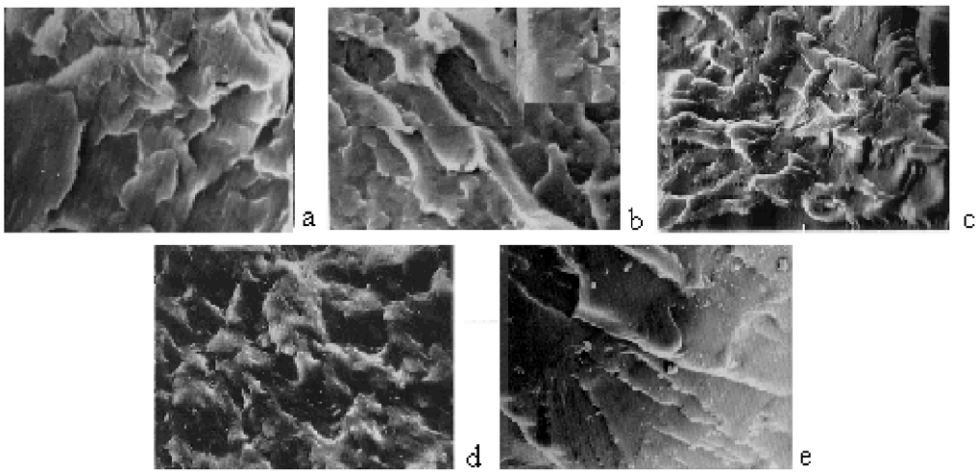

Fig. 6. TEM micrographs of IPNs: (a) PUS10, (b) PUS20, (c) PUS40, (d) PUS60 and (e) PUS80; 10 mm = 5 μm.

The present study has shown that the morphology and properties of IPNs are greatly affected by the reaction of formation of one or both networks in the IPNs.

The morphology for these IPNs were further observed more directly by means of TEM. TEM images appear to exhibit bicontinuous morphology. When thermodynamic forces are dominant result a strong phase separation before the ramification was able to hinder. In this case are situated the samples PUS40 and PUS60 that are representative for strong incompatible polymers. In the case of polymers with a partial miscibility, the phase separation can be avoided, the samples PUS10 and PUS80.

4. Conclusions

The IPNs prepared from the PPU based on castor oil and 2,4-TDI, and different amounts of polydimethylsiloxane (PDMS) are highly incompatible and have a heterogeneous phase morphology. All the IPNs exhibited phase separation with the maximum extent shown at the point of phase inversion.

These materials have interesting individual physical properties, but some IPNs exhibited superior properties than either of the separate networks. Through combination of the amounts of both polymers results new materials, which have good properties. Increasing of the amount of polydimethylsiloxane in the IPNs, produces an increase in the thermal stability. IPNs based on PU and polydimethylsiloxane with an amount loss 40% of PDMS are rigid.

The morphology and properties of IPNs obtained in our study depend upon the degree of phase separation, which is related principally to the miscibility of the polymers.

Possible applications include covering materials for biomedicine's, vibration dampening materials, abrasion and thermal resistant coatings.

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