Semiinterpenetrating Polymer Networks Based on Polyurethane and Polyvinylpyrrolidone. I. Thermodynamic State and Dynamic Mechanical Analysis

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ABSTRACT: Semiinterpenetrating polymer networks (semi-IPNs) based on polyurethane (PU) and polyvinylpyrrolidone (PVP) have been synthesized, and their thermodynamic characteristics, thermal properties, and dynamical mechanical properties have been studied to have an insight in their structure as a function of their composition. First, the free energies of mixing of the two polymers in semi-IPNs based on crosslinked PU and PVP have been determined by the vapor sorption method. It was established that these constituent polymers are not miscible in the semi-IPNs. The differential scanning calorimetry results evidence the T_g of polyurethane and two T_g for PVP. The dynamic mechanical behavior of the semi-IPNs has been investigated and is in accordance with their thermal behavior. It was shown that the semi-IPNs present three distinct relaxations. If the temperature position of PU maximum tan δ is invariable, on the contrary, the situation for the two maxima observed for PVP is more complex. Only the maximum of the highest temperature relaxation is shifted to lower temperature with changing of the semi-IPNs composition. It was concluded that investigated semi-IPNs are two-phase systems with incomplete phase separation. The phase composition was calculated using viscoelastic properties. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 852–862, 2001

Key words: interpenetrating polymer networks; thermodynamic miscibility; free energy of mixing; glass transition; dynamics mechanical spectroscopy; molecular dynamic; structure

INTRODUCTION

Investigations on the interpenetrating polymer networks (IPNs) have been carried out widely by scientists in different countries as evidenced by the large number of reviews and monographs.[1–5]

The formation of the interpenetrating polymer networks is determined by two factors: the kinetics of the chemical reactions and the processes of microphase separation.[6] The miscibility of the constituent components of the IPNs is a main factor in determining the IPNs morphology.[7,8]

It was shown[9] that the buildup kinetics of IPNs and the ratio of curing rates of the network constituents determine the rate and degree of microphase separation in immiscible systems. Many factors play an important role in determining the

properties of IPNs: thermodynamic miscibility of the polymers, overall composition, method of synthesis, crosslink density in both polymers, glass transition temperature, and crystallinity. In the case of highly immiscible polymers, the thermodynamic forces leading to phase separation are so powerful that it occurs before the kinetic processes can prevent it. As a result, poor phase mixing takes place. If polymers with better miscibility are used, there is almost no phase separation, which is effectively controlled by permanent entanglement of the chains. For cases between these two extremes, the result is an intermediate or complex phase behavior of materials. Thus, IPNs with dispersed phase domains ranging from a few micrometers (incompatible) to a few ten nanometers (intermediate) can be obtained.[10]

In this paper the preparation and properties of semiinterpenetrating polymer networks (semi-IPNs) based on polyurethane and polyvinylpyrrolidone are described. The semi-IPNs are the systems consisting of a chemical network and linear polymer. These systems were prepared by the sequential method. First, the polyurethane network was synthesized. Then it was swollen by the monomer vinylpyrrolidone. Swollen polyurethane is a thermodynamically stable system as the swelling in the monomer is a self-governing process. Following that, photopolymerization of vinylpyrrolidone were carried out quickly. As a result, we have received the samples of semi-IPNs with optical transparency.

The aims of the present paper are the detailed investigations of the thermodynamical miscibility of the constituent polymers and the analysis of thermal and dynamic mechanical behavior of the semi-IPNs based on polyurethane and polyvinylpyrrolidone, to study the structure of such materials.

EXPERIMENTAL

Materials

The semi-IPNs were prepared on the basis of the polyurethane (PU) network and linear polyvinylpyrrolidone (PVP). First the polyurethane network was synthesized by a two-step method. The first step was the preparation of the adduct of trimethylol propane and toluylene diisocyanate. Toluylene diisocyanate was distilled on a vacuum line. Trimethylol propane was dried at 308 K

under vacuum. Then trimethylol propane was dissolved in ethylacetate. The adduct of trimethylol propane and toluylene diisocyanate was prepared by reacting 1 equivalent of trimethylol propane (TMP) with 1.5 equivalents of toluylene diisocyanate (TDI) at 338 K. The reaction was carried out until the theoretical isocyanate content was reached, which one was determined by the di-n-butylamine titration method. The second step was the synthesis of the crosslinked polyurethane. The polyurethane network was obtained from poly(diethylene adipate glycol), M_w 2000, and adduct of trimethylolpropane and toluylene diisocyanate (ratio 1:2 g-ekv) at temperature 353 K in a nitrogen atmosphere for 48 h. The poly(diethylene adipate glycol) was degassed at 343 K for 8 h under vacuum before use. Unreacted materials were extracted from the polyurethane network by the Soxhlet extraction method using ethylacetate as a solvent. As result, we have received the polyurethane network of the next structure:
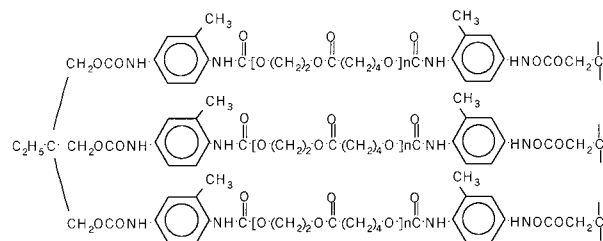
The semi-IPNs were obtained by the sequential method. The polyurethane network was swollen in monomer N-vinyl-α-pyrrolidone:
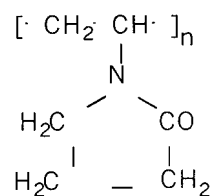
The monomer contained benzoine isobutyl ether as the initiator. The swelling was carried out to the equilibrium state. The N-vinyl-α-pyrrolidone was distilled on a vacuum line before use.

The second polymer polyvinylpyrrolidone was cured by photopolymerization of the monomer, which was carried out in a temperature-controlled chamber for 2 h. The wavelength of UV light was 365 Å.

The semi-IPNs prepared were then held in vacuum 10^{-5} Pa at 373 K for 36 h to reach the constant weight.

By this procedure different semi-IPNs with a wide range of compositions were obtained.

Vapor Sorption

The benzene vapor sorption of semi-IPNs was studied using a vacuum installation and a McBain balance.

From experimental data on benzene vapor sorption by the different polymer systems, we have determined the change $\Delta\mu_1$ in partial free energy of benzene by sorption (dissolution):

$$\Delta\mu_1 = (1/M)RT \ln(P/P_0) \qquad (1)$$

where M is the molecular mass of benzene and P/P_0 is the relative vapor pressure. The value $\Delta\mu_1$ changes with solution concentration from 0 to $-\infty$.

To calculate the free energy of mixing of the polymer components with solvent, we need to know the changes in partial free energy of the polymers (individual polymers and semi-IPNs).

$\Delta\mu_2$ is the difference between the polymer chemical potential in solution of a given concentration and in the pure polymer under the same conditions. $\Delta\mu_2$ for the polymer components have been calculated according to the Gibbs–Duhem equation:

$$\omega_1 \, d(\Delta\mu_1)/d\omega_1 + \omega_2 \, d(\Delta\mu_2)/d\omega_1 = 0 \qquad (2)$$

where ω_1 and ω_2 are respectively the weight fractions of the solvent and of the polymer.

$$\int d(\Delta\mu_2) = -\int (\omega_1/\omega_2) \, d(\Delta\mu_1) \qquad (3)$$

Hence by integration over definite limits, the values $\Delta\mu_2$ have been found from the experimental data.

The average free energy of mixing Δg^m of the solvent with the individual components—that is to say the semi-IPNs of various compositions for solutions of different concentrations—was estimated according to

$$\Delta g^m = \omega_1\Delta\mu_1 + \omega_2\Delta\mu_2 \qquad (4)$$

Differential Scanning Calorimetry Measurements

Differential scanning calorimetry (DSC) measurements were carried out using a calorimeter 2920 TA Instruments. The samples were sealed in aluminum pans and measurements were performed under a high purity continuous helium purge. Samples were subjected to the following thermal cycle: a first heating then cooling and a second heating with a scan rate of 10 K min^{-1} over the temperature range from -140 to 225°C. The T_g was taken as the onset of the change in slope from the plot of heat capacity as function of temperature.

Dynamic Mechanical Analysis Measurements

The dynamic mechanical analysis (DMA) were carried out with a Dynamic Mechanical Thermal Analyzer Type DMA 2980 TA Instruments over the temperature range from -140 to $+240$°C and at fixed frequencies (3, 5, 10, 15, 20 Hz) with a heating rate of 3°C/min. The experiments were performed under tension mode on rectangular specimens ($25 \times 5 \times 1$ mm).

RESULTS AND DISCUSSION

Thermodynamic State of Semi-IPNs

The samples of semi-IPNs based on polyurethane network and polyvinylpyrrolidone are optically clear in all investigated composition range. But it was shown earlier[10–12] that the microphase separation in IPNs and semi-IPNs is incomplete and that the systems have a "frozen" nonequilibrium structure. This nonequilibrium frozen structure is the result of two processes: the chemical reaction of the IPNs formation and the physical process of microphase separation accompanying the reaction. The optical clarity of the samples is not sufficient evidence to conclude about miscibility of the polymer components of the semi-IPNs. To estimate the thermodynamic state of investigated semi-IPN, we calculated the free energy of mixing of the constituent polymers. For this purpose we have studied the vapor sorption of all the samples under investigation. In Figure 1, we show the isotherms of sorption of benzene at 25°C by polyurethane (1), polyvinilpyrrolidone (2), and semi-IPNs of various compositions (3–6). The isotherm of polyurethane (1) has the shape of typical elastomer isotherm. For polyvinylpyrrolidone (2) the sorption is very small in the range of the relative pressure up to 0.5, then it increases very quickly. This behavior is typical for glassy-state polymers. The semi-IPNs behaviors are between these two extremes.

From the experimental data on benzene vapor sorption, we calculated the thermodynamic pa-
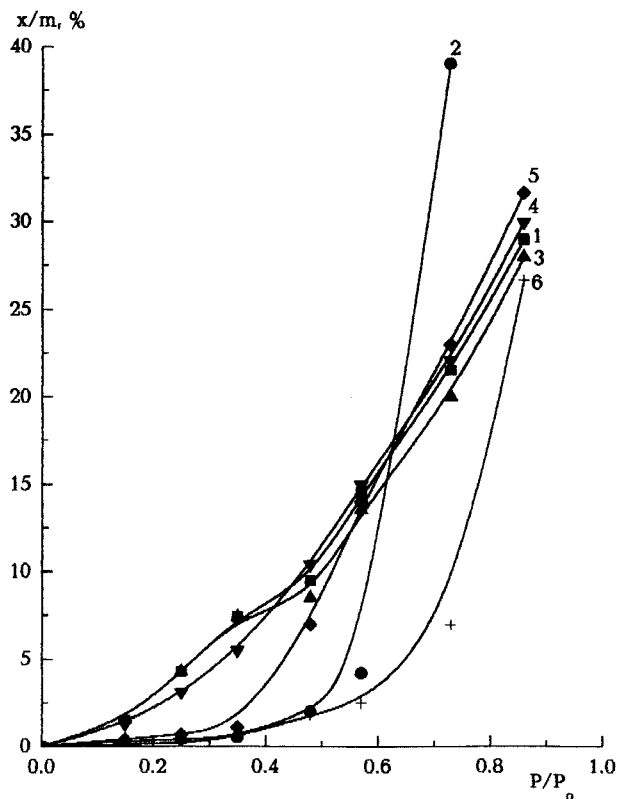
Figure 1 Isotherm sorptions of benzene vapor by polyurethane (1), polyvinylpyrrolidone (2), and semi-IPNs with 13.27% (3), 22.53% (4), 41.03% (5), and 57.38% (6) of polyvinylpyrrolidone. x/m: amount of benzene related to the dry sample; P/P_o: related pressure of benzene.

rameters (the method of calculation has been described in the Experimental section). In Figure 2, we show the change of free energy of mixing of benzene with individual polyurethane (curve 1), with polyvinylpyrrolidone (curve 2), and with semi-IPNs (curves 3–6). We can see that all the studied systems (PU–benzene, PVP–benzene, and semi-IPNs–benzene) are thermodynamically stable [$d^2\Delta g^m/d\omega_2^2 > 0$]. The affinity of benzene for polyvinylpyrrolidone (Fig. 2, curve 2) is higher than for polyurethane (Fig. 2, curve 1). For semi-IPNs, the affinity of benzene becomes higher with increasing of the amount of PVP in the samples (Fig.2, curves 3–6).

From the concentration dependence of the free energy of mixing of benzene and the system components (Fig. 2), using the thermodynamic cycles,[13] we have calculated the changes in free energy of mixing between the polyurethane and polyvinilpyrrolidone in the semi-IPNs with a wide range of composition. The data are presented in the Table I.
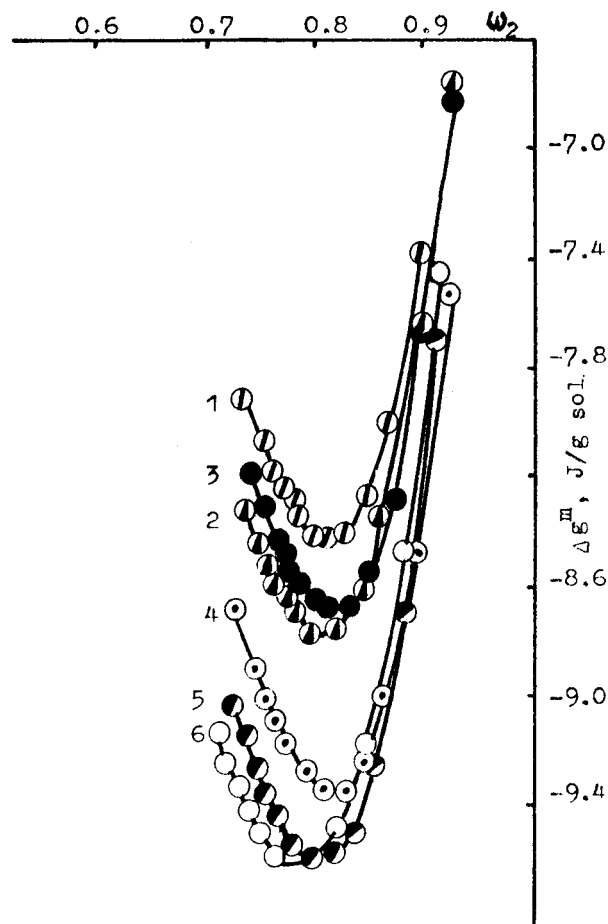
Figure 2 Free energy of mixing Δg^m versus weight fraction of polymer (semi-IPNs) ω^2 with solvent: (1) PU, (2) PVP, (3) semi-IPN with 7.5 % PVP, (4) semi-IPN with 22.53% PVP, (5) semi-IPN with 41.03% PVP, (6) semi-IPN with 57.38% PVP.

We can see that the values of the free energy of mixing are positive. Therefore, the components are immiscible, the whole semi-IPNs being thermodynamically unstable.

Table I Variation of the Free Energy of Mixing Δg^x of Polyurethane and Polyvinylpyrrolidone in the Semi-IPNs

Composition of Semi-IPNs	Δg^x (J K^{-1} g^{-1})
Semi-IPN with 7.05% PVP	+0.47
Semi-IPN with 13.27% PVP	+1.04
Semi-IPN with 22.53% PVP	+1.26
Semi-IPN with 30.35% PVP	+1.52
Semi-IPN with 41.03% PVP	+1.83
Semi-IPN with 57.38% PVP	+2.17

Table II   Glass Transition Temperatures of PU, PVP, and Semi-IPNs Based on PU and PVP

PVP (wt %)	T_g °C PU	T_{g_L}/T_{g_U} °C PVP
0	−22	—
7.05	−21	42–105
13.27	−22	35–138
22.53	−21	45–148
30.35	−25	41–124
41.03	−25	40–125
57.38	−24	37–123
100	—	43–149

DSC Analysis

A summary of the DSC results for the PU, PVP, and semi-IPNs is presented in Table II. In spite of the optical transparency of the semi-IPNs samples, we can observe three T_g in these samples. At low temperatures we have the T_g of individual polyurethane (−22°C). The T_g of PU in the semi-IPNs is practically the same as of individual polyurethane (Table II). This means that polyurethane glass transition is not influenced by addition of PVP.

Pure PVP presents two thermal transitions called T_g, one at about $T = 43$°C, which we called lower T_g (T_{g_L}), and a second one generally reported in the literature[14] at $T = 149$°C, which we called upper T_g (T_{g_U}). Contrary to the T_g values of PU and T_{g_L} values of PVP, the T_{g_U} values of PVP in semi-IPNs change with PVP content in the samples. The T_{g_L} is to be related to the classical glass transition of the PVP "free" chains associated with cooperative motion of long chain segments. However, we think that the so-called upper T_g (T_{g_U}) results of the possible intra- or interchain coupling–decoupling effect between polyvinylpyrrolidone chains is due to the polarity of the heterocyclic pendant group and hydrogen-bonding formation. The consequence is that the upper T_g (T_{g_U}) can be interpreted as a conformational disorder or disorganization (softening) of local order due to these couplings between PVP chains. In the case of the IPNs, the coupling effect can be considered between the PVP chains but also between PVP and PU chains.

So, we can conclude, that investigated semi-IPNs are two phases systems with PVP–PVP and/or PU–PVP interactions according their compositions. This result is also in agreement with thermodynamic investigation and will be confirmed by the following dynamic mechanical mea-surements of these semi-IPNs. It was shown above that the investigated semi-IPNs are thermodynamically immiscible. But the changing of the upper Tg of PVP in semi-IPNs with content of PVP (Table II) can demonstrate also that microphase separation is incomplete in these systems.

When the separation into two phases occurs in the semi-IPNs : one phase - polyurethane phase-has always the same T_g for all investigated semi-IPNs and for pure polyurethane, but the second polyvinilpyrrolidone phase has an upper T_g that shifts to lower temperature with changing of the composition. So, we can conclude that this phase is not pure PVP phase, but the solution of the component 1 into component 2 of the semi-IPNs. Introduction of polyurethane chains decreases or changes the interactions or plastisized the PVP phase.

In conclusion, we can say that upper T_g of PVP is sensitive to the introduction of polyurethane chains, which will change the possibility of interactions between the chains of PVP.

Viscoelastic Properties

DMA studies of IPNs can be used to characterize indirectly microstructure of the materials and to establish structure–property relationships. DMA will also allow us to determine the damping characteristics of such systems.[15]

Figure 3 shows the dependence of Log storage modulus E' (curve 1), the loss modulus E'' (curve 2), and tan δ (loss factor) (curve 3) for investigated PU in temperature range −150−+200°C at a frequency of 1 Hz. At low temperatures (−120°C) we observe a weak loss modulus relaxation, which correlates with the β-relaxation process in the polyurethane. The β-relaxation process is due to the rotation of the —O—CO—$(CH_2)_4$— ester groups in the polydiethylene adipate glycol, which correspond to the soft block of the polyurethane. As the temperature increases, a second relaxation mechanism appears, which is shifted to higher temperatures with increasing frequencies. The position and the shape of this broad loss peak allow us to relate it to the main glass–rubber transition (α-relaxation) of the polyurethane network. The corresponding variation of Log E' is in accordance with such α-relaxation and decreases over about 3 decades of amplitude.

Figure 4 shows the Log storage modulus E' (curve 1), the loss modulus E'' (curve 2), and tan δ (loss factor) (curve 3) for pure PVP in temperature
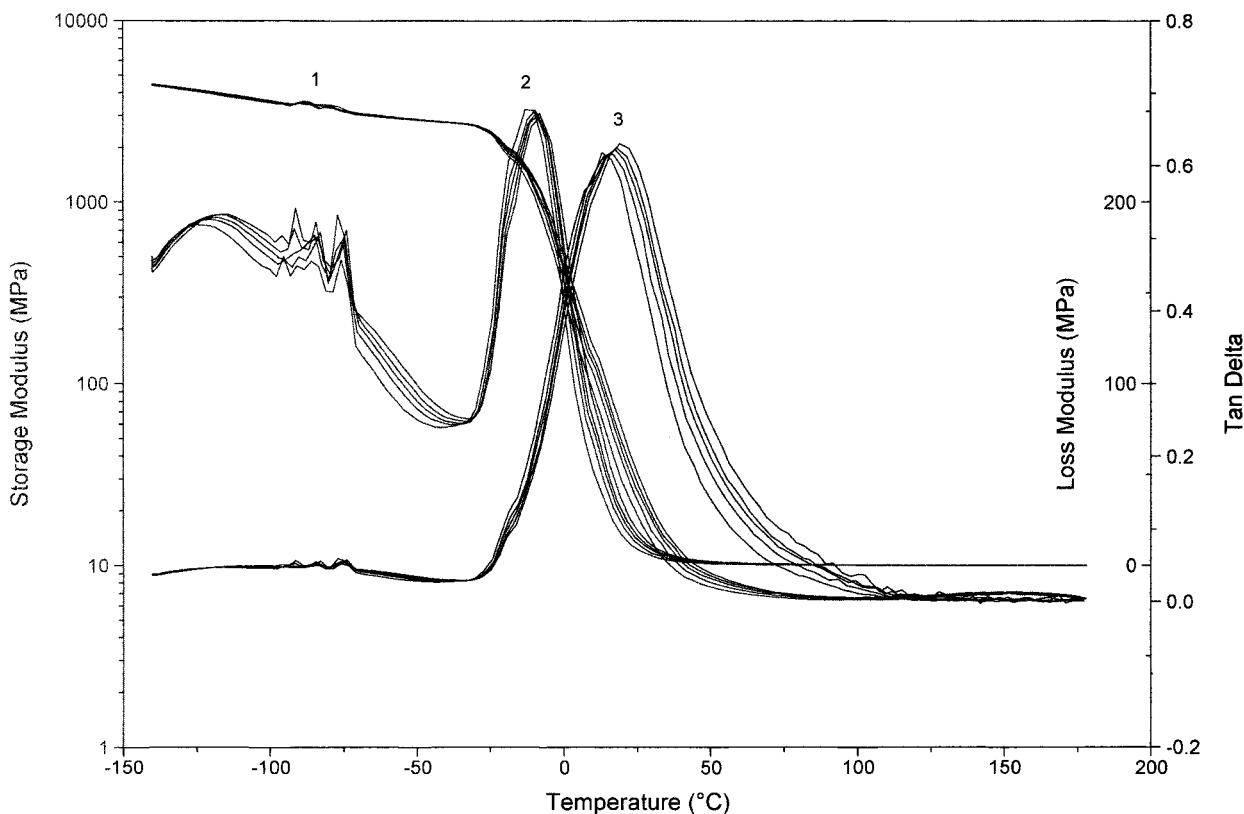
Figure 3 Dependence of the Log storage modulus (1), loss modulus (2), and loss factor tan δ (3) versus temperature for PU sample in DMA measurements.

range −150−+200°C at a frequency of 1 Hz. At low temperatures (−90°C) we observe a weak loss modulus relaxation, which correlates with the β-relaxation process in the polyvinylpyrrolidone. The β-relaxation process is certainly due to the rotation of the pendant heterocycle group.

As the temperature increases, two other relaxation mechanisms appear clearly on curve 3 of tan δ, related with a good agreement to the two thermal transitions obtained in DSC results. These relaxations both shift to higher temperatures with increasing frequencies. So the position and the shape of these broad loss peaks allow us to relate them to the main glass–rubber transition (αl-relaxation) of the polyvinylpyrrolidone chains and to the upper glass–rubber transition (αu-relaxation), which has been related to the glass transition of intra- or interdependent PVP chains through strong polar interactions between their heterocyclic pendant groups.

The corresponding variation of Log E' (Fig. 4, curve 1) is in accordance with such double α-relaxations and decreases in two corresponding steps over about 4 decades of amplitude. It is

noticeable that Log E' decreases only on one decade at (αl) and then strongly decreases when the second (αu) relaxation appears. At this point, all the interactions vanish in the materials and the modulus decreases stiffly. It is why we do not observe on loss modulus curve 2 the αu-relaxation. This result is also in agreement with the fact that the amplitude of tan δ is higher for αu-relaxation than for αl-relaxation. This last one is due to the general motion of the PVP free chains, restricted nevertheless by the PVP chains, which present intra- or intercouplings. When T_{g_U} appears, the associated αu-relaxation corresponds to the motion of the decoupled chains. Its amplitude is then higher than the one of αl because all the chain segments of PVP chains are allowed to be involved in the αu-relaxation as all the interactions are broken.

So the dynamic mechanical results confirm quite well the existence of two T_g's for polyvinylpyrrolidone, which is not obvious from the DSC measurement as the lower T_g is not easy to detect on thermogram and is not mentioned in the literature. The upper T_g determination seems
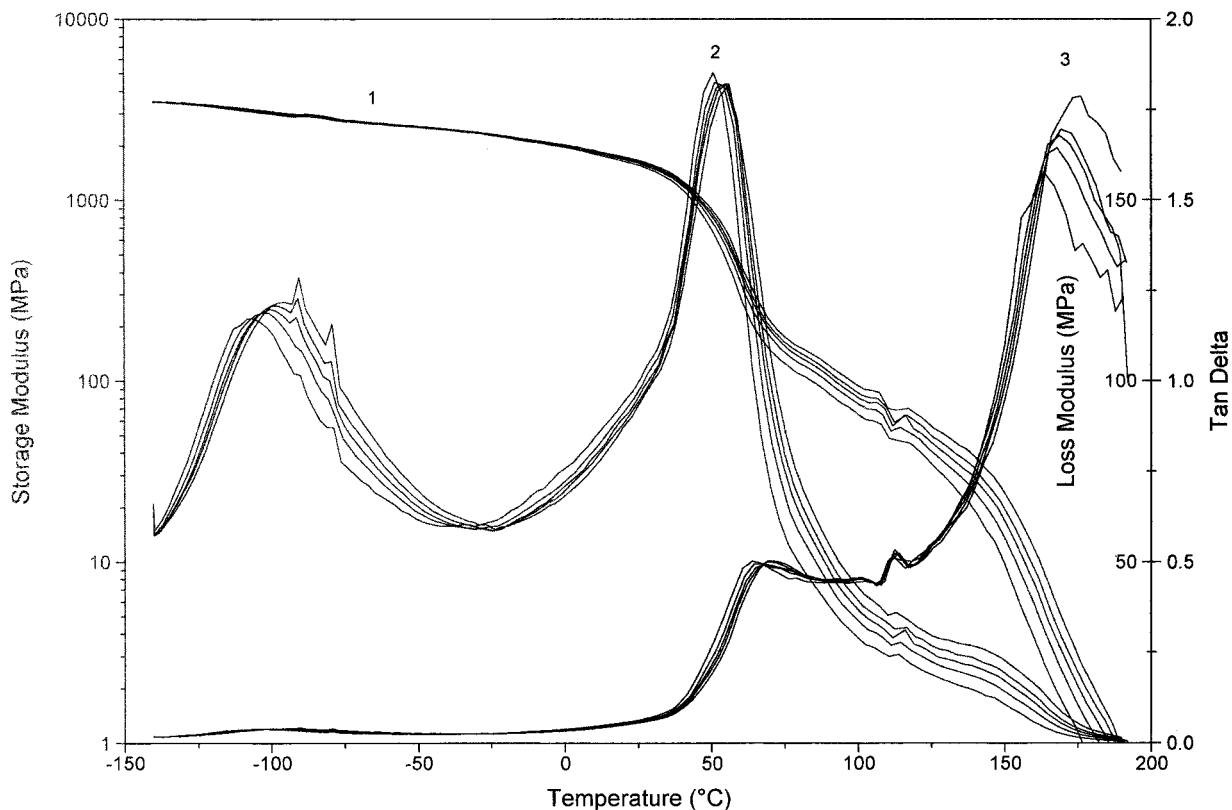
Figure 4 Dependence of the Log storage modulus (1), loss modulus (2), and loss factor tan δ (3) versus temperature for PVP sample in DMA measurements.

also influenced by the water uptake of the materials and the aging effect.

Figure 5 shows the Log storage modulus E' (curve 1), the loss modulus E'' (curve 2), and tan δ (loss factor) (curve 3) for semi-IPN containing 41.03% of polyvinylpyrrolidone. This picture is typical for all investigated semi-IPNs. At low temperatures we observe the broad loss modulus peak and tan δ peak, which correlate with the β-relaxation processes in polyurethane and in polyvinylpyrrolidone as well without possibility to distinguish them really. In the temperature range of −25–+25°C we can see the second peak on the curves loss modulus and tan δ and the corresponding step on of Log storage modulus curve, which is connected with α-relaxation (glass–rubber transition) in polyurethane networks (see Fig. 3).

With increasing of the temperature, two other relaxations (αl and αu) appear on the curves of storage modulus and tan δ. Their positions and magnitudes allow us to relate them to the two glass–rubber transitions so-called T_{g_L} and T_{g_U} of the polyvinylpyrrolidone.

We have investigated 6 samples of semi-IPNs with different concentrations of polyvinylpyrrolidone from 7.05 up to 57.38 %. In Figure 6 the variation of Loss factor vs temperature data for investigated semi-IPNs are presented in the temperature range of −75 up to 175°C, corresponding to the α-relaxation temperature domains of the two components. We can see that the amplitude of the α-polyurethane relaxation decreases in semi-IPNs by increasing the amount of polyvinylpyrrolidone but the temperature position of this relaxation is invariable. This means that we have a pure PU phase since PVP introduction has no effect on the properties of the PU phase.

The amplitude of the highest α-relaxation—relaxation αu of polyvinylpyrrolidone—decreases with the increase of the amount of PU in semi-IPN; the position of this relaxation also shifts to lower temperatures (Fig. 6). These results are in accordance with the DSC results. Additionally, we observe that it is difficult to see clearly the αl relaxation, which contributes as a shoulder of the αu- relaxations up to the 22.53% content of PVP in IPN and then which appears as a single relax-
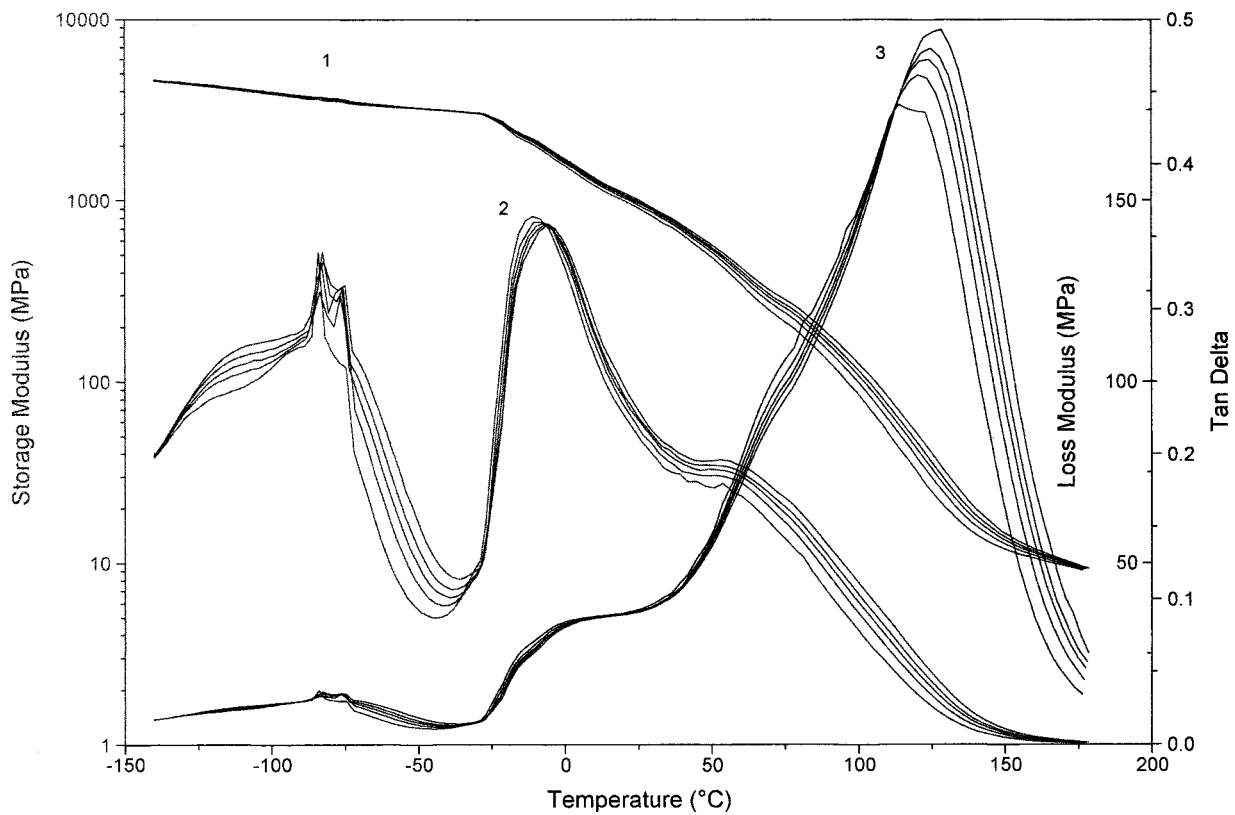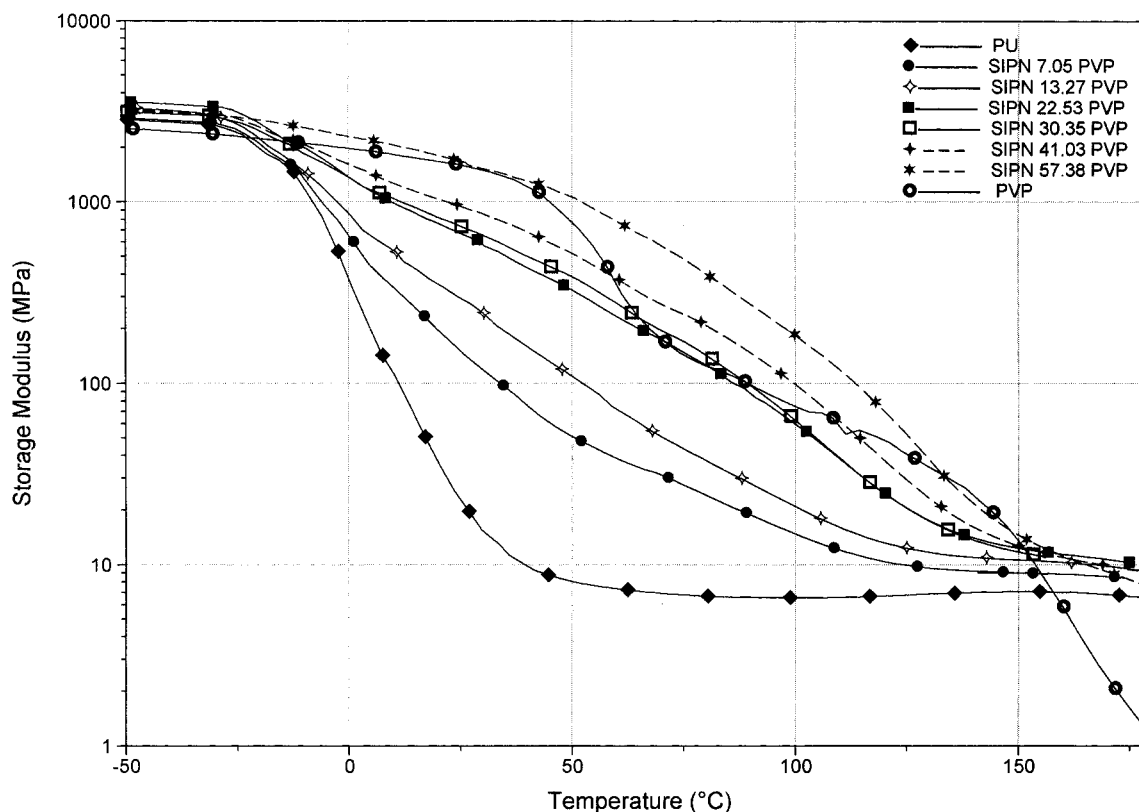
Figure 5 Variation of the Log storage modulus (1), loss modulus (2), and loss factor tan δ (3) versus temperature for the semi-IPN with 41.03% PVP in DMA measurements.
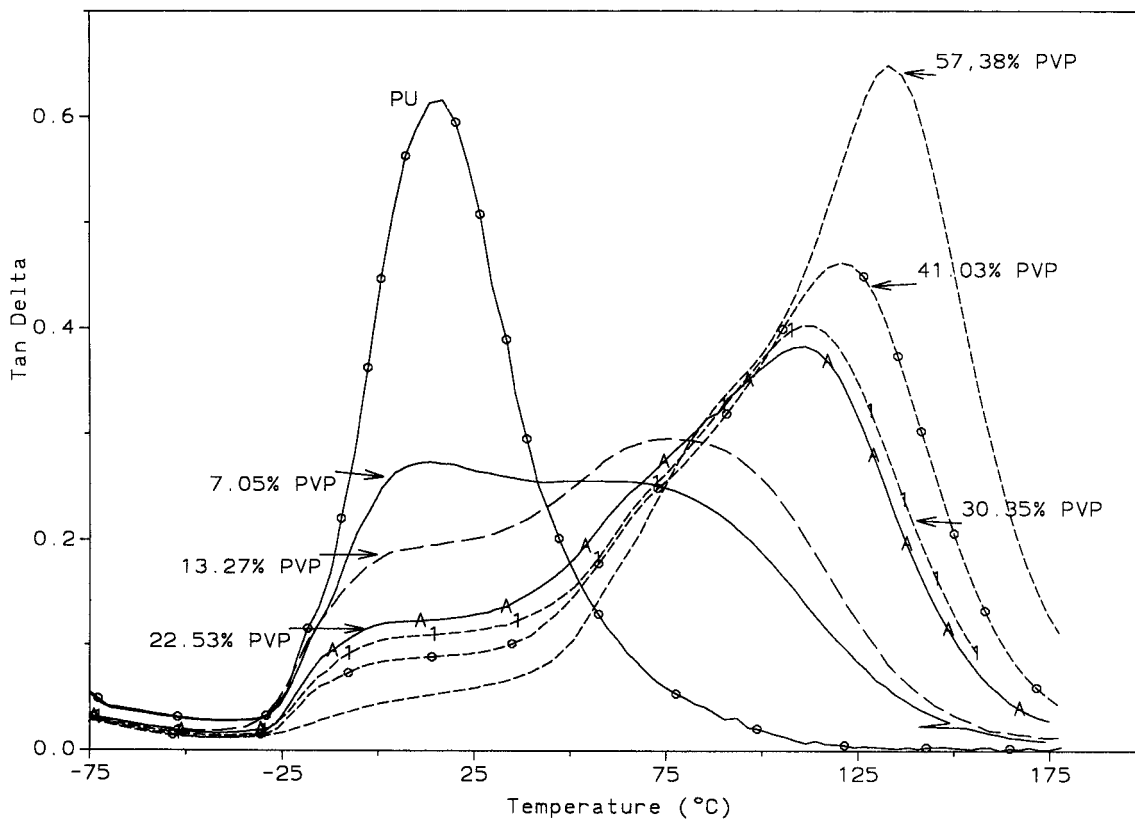
Figure 6 Dynamic mechanical measurements of loss factor versus temperature data for PU and for semi-IPNs with different amounts of PVP.

Figure 7   Log storage modulus versus temperature data for PU, PVP, and semi-IPNs with different amounts of PVP.

ation when the αu-relaxation does not exist anymore for low content PVP in IPN as not enough interactions are possible between PVP chains to get such a relaxation.

So, we must conclude that the investigated semi-IPNs are two-phase systems but their phase separation is not complete since for low content of PVP in PU we observe an influence on the end of α-PU relaxation and on the beginning of αl-PVP relaxation.

The storage moduli of the investigated semi-IPNs (Fig. 7) reflected the trends of the loss factor data. The curves of storage moduli have a view of typical two-phase systems with no complete phase separation. There are no two sharp decreases of storage moduli with temperature (only observed for pure PVP). We can observe the increase of the storage moduli of the semi-IPNs with increasing of the amount of polyvinylpyrrolidone in these systems. It corresponds to the reinforcement of the PU.

In Figure 8 are shown the temperature dependencies of the Loss moduli for PU (1), PVP (2), and semi-IPNs with 30.35 (3), 41.03 (4), and 57.38%

(5) presented in the temperature range of -150 up to 175°C corresponding to the β- and α-relaxation temperature domains of the two components. We can see the distinct maximum of the loss modulus for PU and PVP around -100°C, then in the temperature range of $-25-0$°C for α-PU and broad maximum of loss modulus for αl-PVP in the temperature range of $30-100$°C. The amplitudes of the corresponding relaxations of IPN (α-PU and αl-PVP) reflect very well their compositions. In any case, it is not possible to see αu-PVP as the modulus E' decreases strongly above 130°C.

It was shown above (Table I) that the investigated semi-IPNs are thermodynamically immiscible. They have positive values of free energy of mixing between the two constituent polymers. But the microphase separation in the semi-IPNs is incomplete and the systems have a "frozen" nonequilibrium structure. The separation into two phases occurs. But one phase—polyurethane phase—has the same temperature of α-relaxation for all investigated semi-IPNs (Fig. 6) and for pure polyurethane. The same remark concerns
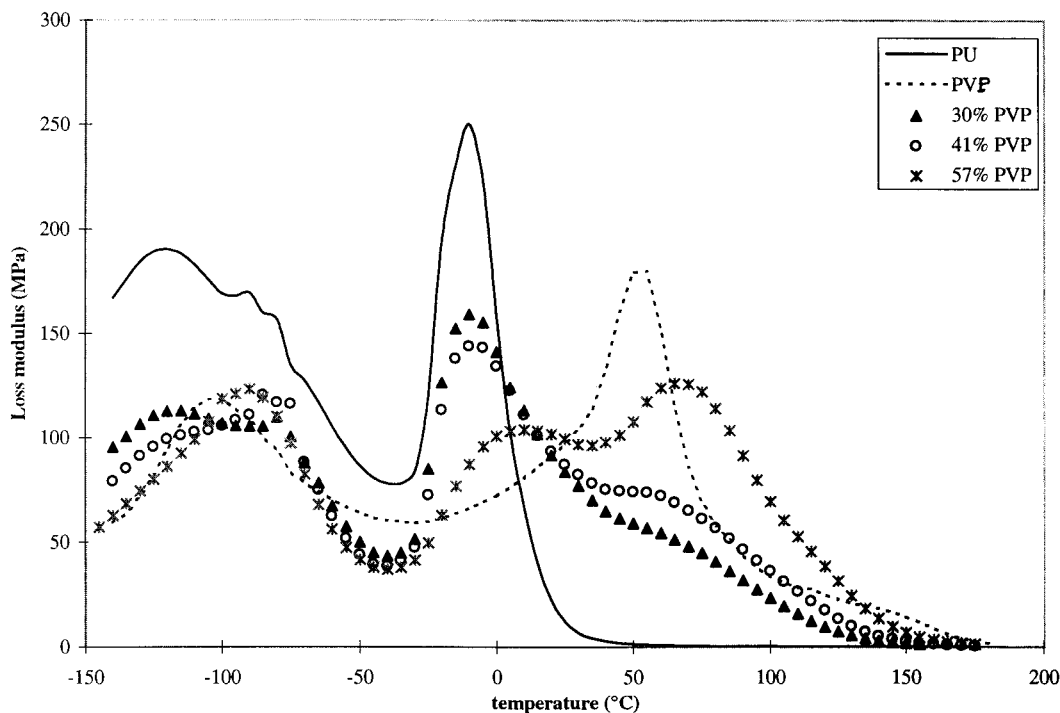
Figure 8 Dependence of the loss modulus versus temperature for PU (1), PVP (2), and semi-IPNs with 30.35% (3), 41.03% (4), and 57.38% (5) of PVP.

the αl-relaxation of PVP, which is not influenced by the IPN formations and which is finally an intrinsic properties of the PVP chains presenting usual T_g corresponding to cooperative motion of chain segments. On the contrary, the αu-relaxation of the second phase in the semi-IPNs—polyvinylpyrrolidone phase—shifts down on the temperature scale with changing of the composition (Fig. 6).

So, we can conclude that this phase is not pure PVP phase, but the solution of the component 1 into component 2 of the semi-IPNs. According to ref. 6, this phase may be considered as an independent quasi-equilibrium semi-IPN. Considering the PVP phase arising in the course of incomplete phase separation as an independent quasi-equilibrium semi-IPN, we can estimate the composition of this phase. For this purpose we have used the Fox equation [16]:

$$1/T_g = \varphi_1/T_{g1} + \varphi_2/T_{g2} \qquad (5)$$

where φ_1 and φ_2 are the volume fractions of the components, T_{g1} and T_{g2} are their glass transition temperatures, and T_g is the glass temperature of compatible blend, which in our case is the glass

transition temperature of the phase enriched in the polyvinylpyrrolidone in the semi-IPNs (T_{g_U}).

From the corresponding data of the glass transition temperatures in the semi-IPNs, the volume fraction of the PVP in the PVP-enriched phase was calculated according to

$$\varphi_2 = (T_{g1}T_{g2} - T_{g2}T_g'')/T_g''(T_{g1} - T_{g2}) \qquad (6)$$

In this equation T_g'' is the glass temperature transition of the polyvinylpyrrolidone in the semi-IPNs (T_{g_U}).

The data of calculations are presented in Table III. From this table, it is seen that the changing of the ratio of the components in the semi-IPNs leads to the differences in the composition of the PVP-enriched phase in the course of formation.

CONCLUSIONS

The thermodynamic state and dynamic mechanical behavior of semiinterpenetrating polymer networks on the basis of crosslinked polyurethane and polyvinylpyrrolidone have been investigated.

Table III   Glass Transition Temperatures and Phase Characteristics for Semi-IPNs of Various Compositions Based on Polyurethane and Polyvinylpyrrolidone

System	T_g (Max of Tan δ) (Polyvinylpyrrolidone) (°C)	Volume Fraction PVP in its Phase (φ_2)
PVP	168	1.000
Semi-IPN with 57.38% PVP	135	0.9742
Semi-IPN with 41.03 PVP	122	0.9603
Semi-IPN with 30.35% PVP	114	0.9501
Semi-IPN with 22.53% PVP	109	0.9430

The free energies of mixing of the semi-IPNs components are positive and depend on the amount of PVP in the semi-IPNs samples. Therefore, the components are immiscible. The different levels of immiscibility in semi-IPNs are connected with the composition variations.

The thermal analysis has evidenced the T_g of PU but first of all two T_g's for PVP. As this point is not clear in literature, the present work is interesting as dynamic mechanical measurements have confirmed these two T_g.

The DMA spectra revealed a pronounced change in the viscoelastic properties of semi-IPNs with different amounts of PVP in the samples. The semi-IPNs have three distinct maxima of tan δ according to the presence of two polymers in their glass temperature domains. The temperature position of PU maximum of tan δ is invariable, but the high amplitude of PU relaxation becomes essentially lower in semi-IPNs with increasing of the amount of PVP in the systems. The highest maximum of tan δ of PVP for α-relaxation is shifted on the temperature scale to higher temperature and its amplitude increased with the amount of PVP in the semi-IPNs.

These results suggest that the studied semi-IPNs are two-phase systems with incomplete phase separation. The different levels of immiscibility lead to the different degree of phase separation in the semi-IPNs with different compositions.

The phase composition was calculated using the viscoelastic properties of semi-IPNs. It was shown that the phase of PVP in semi-IPN is not pure PVP phase, but the solution of the component 1 into component 2 of the semi-IPNs.

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