

Semi-Interpenetrating Polymer Networks Based on Polyurethane and Polyvinylpyrrolidone. II. Dielectric Relaxation and Thermal Behaviour

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ABSTRACT: Semi-interpenetrating polymer networks (semi-IPNs) based on crosslinked polyurethane (PU) and linear polyvinylpyrrolidone (PVP) were synthesized, and their thermal and dynamic mechanical properties and dielectric relaxation behavior were studied to provide insight into their structure, especially according to their composition. The differential scanning calorimetry results showed the glass transitions of the pure components: one glass-transition temperature (T_g) for PU and two transitions for PVP. Such glass transitions were also present in the semi-IPNs, whatever their composition. The viscoelastic properties of the semi-IPNs reflected their thermal behavior; it was shown that the semi-IPNs presented three distinct dynamic mechanical relaxations related to these three T_g values. Although the temperature position of the PU maximum $\tan \delta$ of the α -relaxation was invariable, on the contrary the situation for the two maxima observed for PVP was more complex. Only the maximum of the highest temperature relaxation was shifted to lower temperatures with decreasing PVP content in the semi-IPNs. In this study, we investigated the molecular mobility of the IPNs by means of dielectric

relaxation spectroscopy; six relaxation processes were observed and indexed according to the increase in the temperature range: the secondary β -relaxations related to PU and PVP chains, an α -relaxation due to the glass-rubber transition of the PU component, two α -relaxations associated to the glass-rubber transitions of the PVP material, and an ionic conductivity relaxation due to the space charge polarization of PU. The temperature position of the α -relaxation of PU was invariable in semi-IPNs, as observed dynamic mechanical analysis measurements. However, the upper α -relaxation process of PVP shifted to higher temperatures with increasing PVP content in the semi-IPNs. We concluded that the investigated semi-IPNs were two-phase systems with incomplete phase separation and that the content of PVP in the IPNs governed the structure and corresponding properties of such systems through physical interactions. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1191–1201, 2003

Key words: interpenetrating networks (IPN); glass transition; dielectric properties; molecular dynamics; mechanical properties

INTRODUCTION

Investigations on interpenetrating polymer networks (IPNs) have been carried out widely by scientists in various countries as evidenced by a number of reviews and monographs.^{1–5}

The synthesis of IPNs is determined by two factors: the kinetics of the chemical reactions and the processes of microphase separation.⁶ The miscibility of the con-

stituent components of the IPNs is very important in the determination of the IPN morphology.^{7,8}

It was shown⁹ that the kinetics of the reaction of formation of the IPNs and the ratio of curing rates of the constituents of the networks determine the rate and degree of microphase separation in immiscible systems. Many factors play an important role in the determination of the properties of IPNs: the method of synthesis, overall composition, miscibility of the polymers, crosslink density in both polymers, crystallinity, and glass-transition temperature (T_g). 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, little phase mixing takes place. If polymers with better miscibility are used, there is almost no phase separation, which is effectively controlled by the permanent entanglement of the chains. For cases between these two extremes, an

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over a temperature range from -140 to 240°C and at fixed frequencies of 3, 5, 10, 15, and 20 Hz at an heating rate of 3°C min^{-1} . The experiments were performed under tension mode on the samples ($25 \times 5 \times 1$ mm).

DEA relaxation spectroscopy

DEA measurements were carried out with a DEA analyzer (DEA 2970, TA Instruments) in a temperature range from -150 to 250°C and at frequencies from 10 to 5×10^4 Hz at a heating rate of 3°C min^{-1} under dry nitrogen. The ceramic parallel plates sensors were used with gold electrodes. A 300-N compression force between the ceramic sensors was also applied. Samples were placed in a glass bell jars under a nitrogen gas flow to avoid oxidation during the increase in temperature.

Particular attention was given to the presence of water in the PVP sample. It is known that PVP is a hydroscopic polymer with about 15% water at usual conditions.¹² So, it was important to dry the PVP sample at 80°C for 48 h under a vacuum before the measurements. In the case of IPNs, PVP was protected by PU from the atmospheric water. So, the semi-IPNs based on PU and PVP were not hydroscopic materials, and water uptake was preserved.

RESULTS AND DISCUSSION

The relaxation behavior of the materials was studied by DMA and DEA spectroscopies and was related to the thermal transitions of pure polymers and semi-IPNs based on these polymers.

DMA and DEA studies of IPNs have been used to indirectly characterize the microstructure of pure polymers and IPN derivatives to establish structure-property relationships in such systems.¹³

Thermal analyses

DSC measurements were carried out on the different compositions of the samples, and a summary of the DSC results for PU, PVP, and the semi-IPNs is presented in Table I. Despite the optical transparency of the semi-IPN samples, usually indicating at this scale a homogeneous material, we observed three T_g 's in these samples. The T_g of PU in the semi-IPNs was practically the same as for the pure PU. This meant that the PU glass transition was nearly not influenced by the addition of PVP.

Pure PVP presented two T_g , one at about 43°C , the so called lower glass-transition temperature (T_{gl}), and a second one at 149°C , the so-called upper glass-transition temperature, (T_{gu}); (Table I). The situation with the T_g of PVP was not clear enough from the literature.^{14–17} D. W. V an Krevelen¹⁴ gave two values: 145

and 175°C . In the handbook,¹⁵ the T_g values of PVP are given as 54 and 86°C . In ref. ¹⁶, the T_g of PVP measured by DSC is reported as 180°C . Nishio et al.¹⁷ gave the T_g for PVP as 150°C . PVP is known as an amorphous polymer.¹² However, an investigation of PVP carefully done by wide-angle X-ray diffraction allowed Nishio et al.¹⁷ to conclude that "PVP is predominantly amorphous, notwithstanding the presence of a phase of low regularity in the pure film and blends containing a large amount of PVP. In this phase PVP molecules are arranged with chain-to-chain lateral ordering to assume a pseudohexagonal packing."

So, as shown in ref. 17; the structure of PVP is not homogeneous; it consists of two parts: an amorphous part and a part with low regularity. The T_{gl} measured in our investigation was perhaps related to the motion of the chain segments in the amorphous part of PVP. We think that T_{gu} in our investigation dealt with motion of chain segments in the ordering part of PVP. This ordering part was the result of interchain or intrachain coupling of the PVP chains due to the polarity of the pendant groups and intrahydrogen bonding formation. This ordering part in the structure of PVP we observed in the micrographs done by scanning electron microscopy.¹⁸

As shown in the Table I contrary to the T_g value of PU and the T_{gl} value of PVP, the T_{gu} values of PVP in the semi-IPNs changed with the PVP content in the samples. So, we concluded; that the investigated semi-IPNs were two-phase systems with a PU-PVP balance and PVP-PVP physical interactions according their compositions. This result is also in agreement with thermodynamic investigation and was confirmed by dynamic mechanical measurements of these semi-IPNs, as reported in a previous article.¹¹

It was shown¹¹ that the investigated semi-IPNs were thermodynamically immiscible. Therefore, the change in the values of the T_{gu} of PVP in the semi-IPNs with content of PVP (Table I) also demonstrated that microphase separation was incomplete in such systems.

When the phase separation occurred in the semi-IPNs: one phase, the PU phase was always the same T_g for all of the investigated semi-IPNs and the pure PU, but the second phase, the PVP phase, had a T_{gu} that shifted to lower temperatures with changes in the composition. So, this phase was not a pure PVP phase but a solution of the component PU into the component PVP of the semi-IPNs.

We concluded that the T_{gu} of PVP was sensitive to the introduction of the PU chains in PVP, which seemed to decrease or to change the possibility of the interactions between PVP chains and, consequently, plastisized the PVP phase.

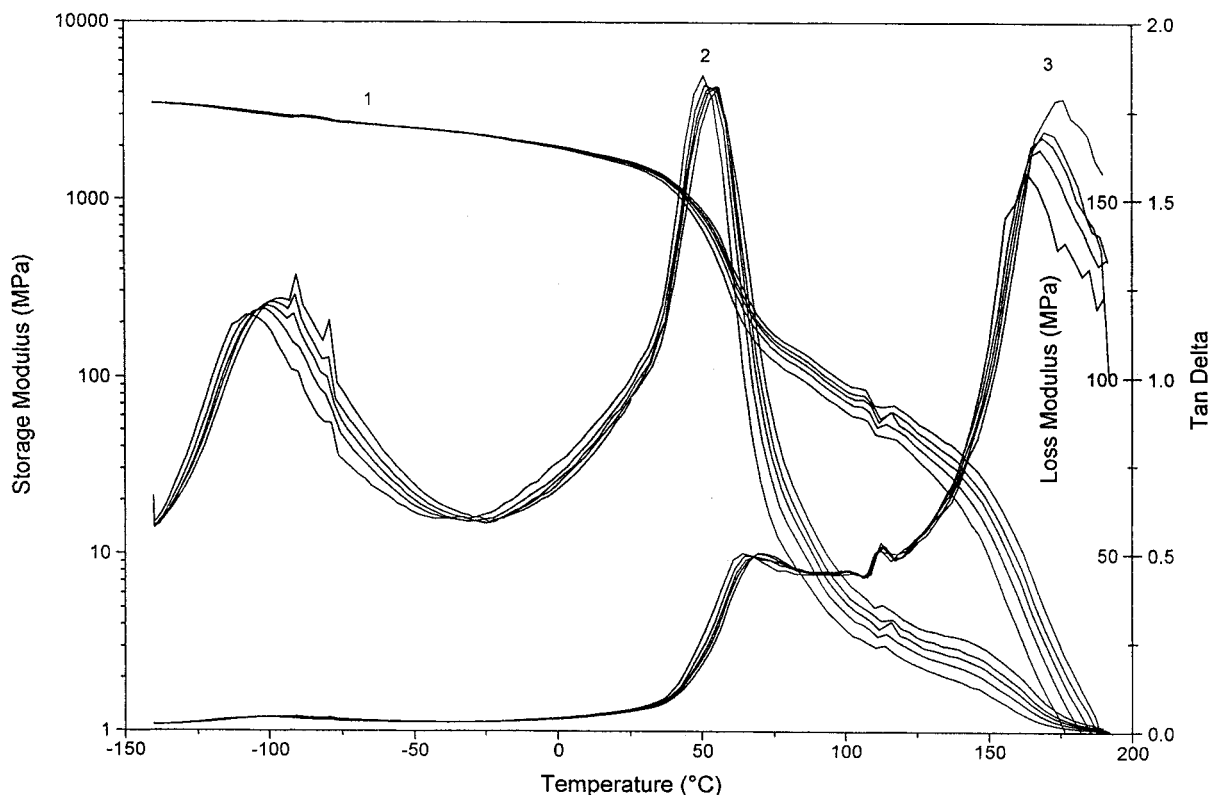


Figure 1 Dependence of (1) $\log G'$, (2) G'' , and (3) $\tan \delta$, versus temperature for the PVP sample in DMA measurements.

Relaxation behavior

In the next two sections, the results obtained by each relaxation method are presented separately; within each section, the relaxation process is described in order of increasing temperature.

Dynamic mechanical spectroscopy

First, we studied the pure PU network by DMA at a low temperature.¹¹ It presented a weak loss modulus (G'') relaxation, which correlated with the β -relaxation process in PU. It was related to the motion of the $-(\text{CH}_2)_4-\text{COO}-$ groups in the poly(diethylene adipate glycol) chain units, which corresponded to the soft block segments of PU.¹⁹ A second relaxation mechanism appeared at higher temperatures and was related to the main glass-rubber transition (α -relaxation) of the PU network according to its position and its shape.²⁰ The corresponding decrease of the logarithm of the storage modulus (G') over about 3 decades of amplitude were in accordance with such α -relaxation.

It is important to report in this article the detailed results concerning the other pure component PVP as it governed the main properties of these IPN systems. Figure 1 shows the $\log G'$ (curve 1), G'' (curve 2), and loss factor; $\tan \delta$ (curve 3) for pure PVP in the temperature range -150 to $+200^\circ\text{C}$. At low temperatures (-90°C , 10 Hz), we observed a weak G'' relaxation, which dealt with the β -relaxation

process in PVP.¹⁹ In this case, the β -relaxation process was certainly due to the motion of the pyrrolidone groups in the amorphous part of PVP.

As the temperature increased, two other relaxation mechanisms appeared clearly on the curve of $\tan \delta$, corresponding to good agreement with the two thermal transitions obtained in the DSC results. These relaxations both shifted to higher temperatures with increasing frequencies. So the position and the shape of these broad loss peaks allowed us to relate them to the main glass-rubber transition (α_T -relaxation) of the PVP chains and to the upper glass-rubber transition (α_U -relaxation) of intradependent or interdependent chains through strong polar interactions between the pendant groups of the PVP chains.

The corresponding variation of $\log G'$ (Fig. 1, curve 1) was in accordance with such double α -relaxations and decreases in two corresponding steps over about 4 decades of amplitude. $\log G'$ decreased only on 1 decade at α_T and then strongly decreased when the second α_U -relaxation appeared. At this moment, all of the interactions vanished in the materials, and the modulus decreased stiffly. This effect explained why the α_U -relaxation was not observed on G'' curves. We, nevertheless, saw a small shoulder.

So, the DMA results confirmed quite well the existence of two T_g for PVP. This point is very important because until now, results in the literature have not

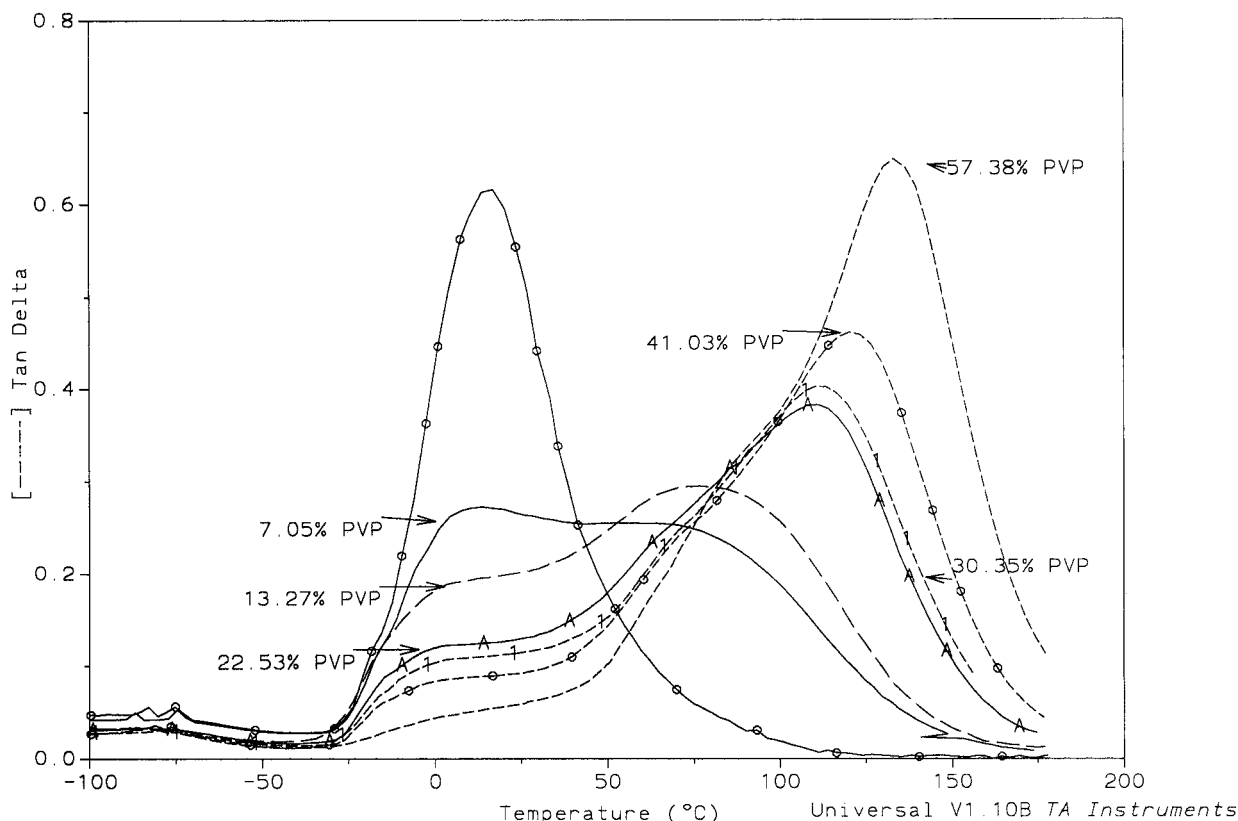


Figure 2 Dynamic mechanical measurements of $\tan \delta$ versus temperature for PU and for semi-IPNs with different amounts of PVP.

clearly indicated the existence of the T_{g1} of PVP, which is not easily detected on thermograms.

We investigated six samples of semi-IPNs with different concentrations of PVP from 7.05 to 57.38%. The investigated semi-IPNs presented the typical previous features of the two pure components, PU and PVP, with more or less emphasis of the corresponding relaxations according their compositions. We first observed a β -relaxation at a low temperature related to local motions of the chain as described in ref. 11.

In Figure 2, the variations in $\tan \delta$ versus temperature for the investigated semi-IPNs are presented in the temperature range -100 to 175°C corresponding to the α -relaxation temperature domains of the two components. The amplitude of the so-called α -relaxation of PU decreased in semi-IPNs with increasing amounts of PVP. However, the temperature position of this relaxation was invariable and corresponded to the motion of the PU chains, which were not in close interaction with the PVP one.

The amplitude of the highest α -relaxation, the α_{ii} -relaxation of PVP, decreased with increasing amount of PU in the semi-IPNs, and the position of this relaxation also shifted to lower temperatures in accordance with the DSC results. Such dependence demonstrated what was previously mentioned about the evolution of the T_{gii} . It is reasonable to think that a bigger amount of PU

changed the properties of PVP through modification of its interchain or intrachain coupling. If the PU chains could also establish some physical interactions with the PVP one and moderate the chain mobility of PVP, this would explain the evolution of the amplitude of the α_{ii} -relaxation of PVP. As a consequence, the α_{ii} -relaxation of PVP shifted to a lower temperature as PVP content decreased, and its amplitude decreased when the interactions in the PVP chains were destroyed by PU.

Additionally, it was difficult to clearly see the α_I -relaxation, which contributed a shoulder to the α_{ii} -relaxations from 57.38 to 22.53% content of PVP in IPNs. Then, the α_I -relaxation related to the T_g of PVP appeared only as a single relaxation for a low content of PVP in the semi-IPNs; in this case, there were not enough interactions between the PVP chains to also get an α_{ii} -relaxation.

As a conclusion of these measurements, it was clear that the investigated semi-IPNs were two-phase systems, but their phase separation was not complete as the α_{ii} -relaxation of PVP shifted so much to a lower temperature with addition of PU.

DEA relaxation spectroscopy

It was interesting to investigate the DEA behavior of the pure components and the semi-IPNs in comple-

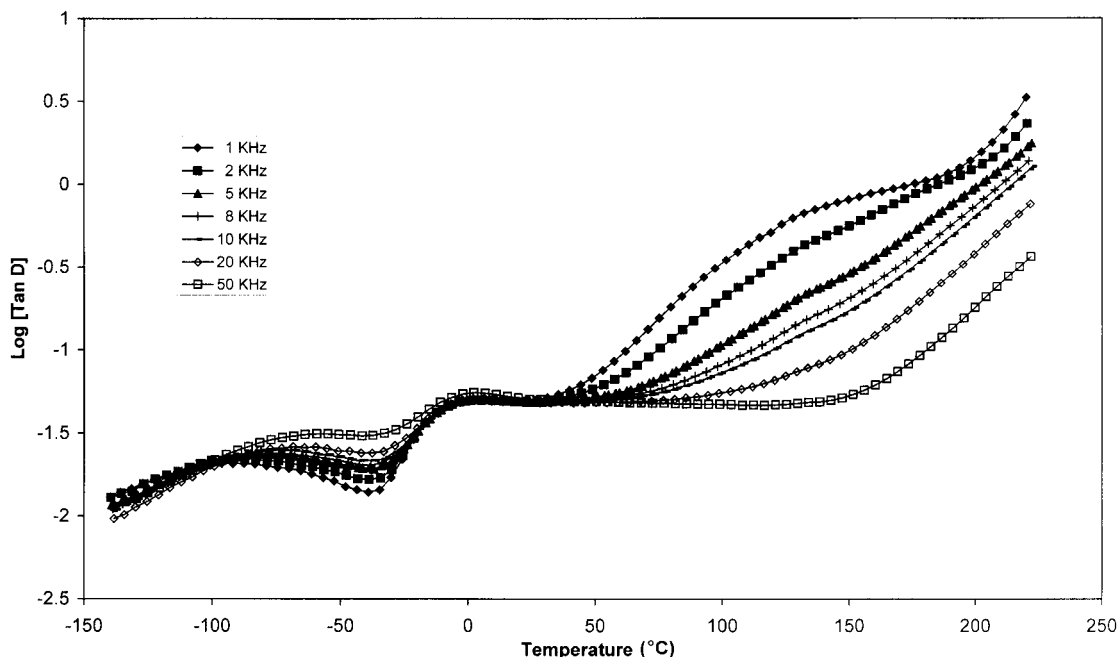


Figure 3 Logarithm of the DEA $\tan \delta$ versus temperature for the PU network at frequencies from 10^3 to 5×10^4 Hz.

mement to mechanical analysis because DEA spectroscopy is a very sensitive method for the analysis of such polar systems. The chain relaxation and the influence of phase separation have to be particularly shown when the composition of the system varies.

The DEA spectra of Figures 3–6 in a wide range of temperatures (-150 to 250°C) and frequencies (10 to 5×10^4 Hz) display all of the relaxation processes of the semi-IPN materials. As DEA spectroscopy is more

sensitive compared to DMA, it was possible to find evidence for six distinct relaxations in the studied components.

Figures 3 and 4 show the logarithm the DEA of $\tan \delta$ [ε'' (loss factor)/ ε' (permittivity)] versus temperature and electric modulus (M'') versus temperature for the PU network.

In order of increasing temperature, the first relaxation, called the β -relaxation, process (-100 to

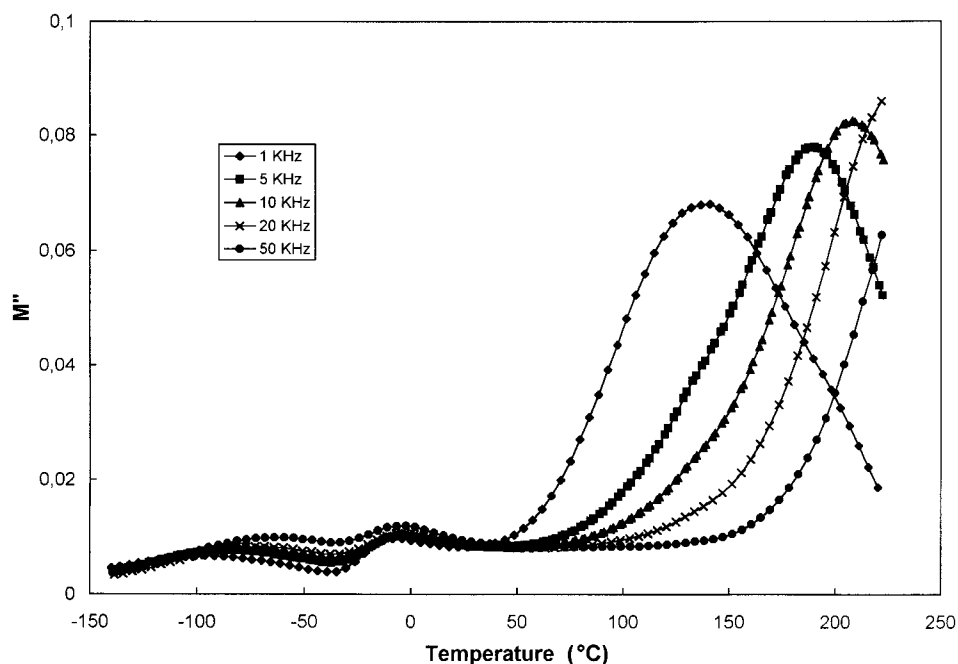
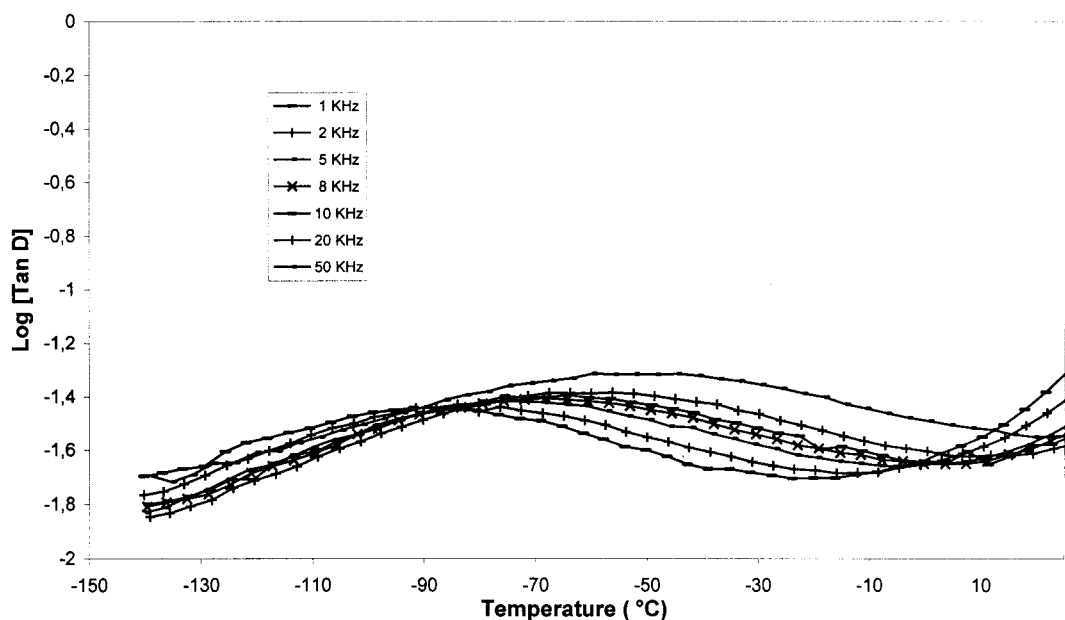
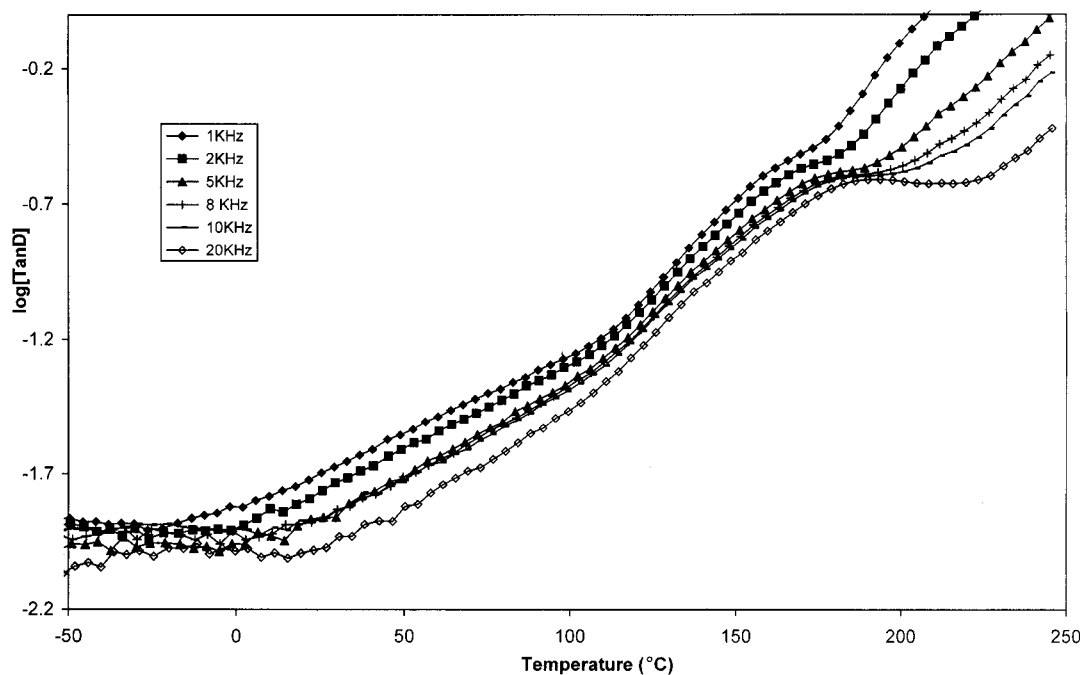


Figure 4 Temperature dependence of M'' for the PU network at frequencies from 10^3 to 5×10^4 Hz.



(a)



(b)

Figure 5 Logarithm of the DEA $\tan \delta$ versus temperature for PVP measured at frequencies from 10^3 to 5×10^4 Hz and temperatures from (a) -150 to -25°C and (b) -50 to 250°C .

-50°C), shown in Figure 3, for the pure PU network was observed and shifted to higher temperatures with increasing frequencies. This β -relaxation process was assigned to the local fluctuations of the $-(\text{CH}_2)_4-\text{COO}-$ groups in the poly(diethylene adipate glycol), which corresponded to the soft block segments of the PU.²⁰ As the temperature increased, a second relaxation mechanism the so-called α -relaxation, appeared on the DEA spectra of PU (-25 to

25°C) and was correlated to the main glass-rubber transition of the PU network.

At high temperatures and low frequencies, we observed a third very intensive relaxation process combined with a conduction effect, the temperature position of which strongly depended on frequency. These phenomena, presented in Figure 4, in the modulus plot were effectively very sensitive to frequency, as a shift of about 80°C was observed between the 1 and 5

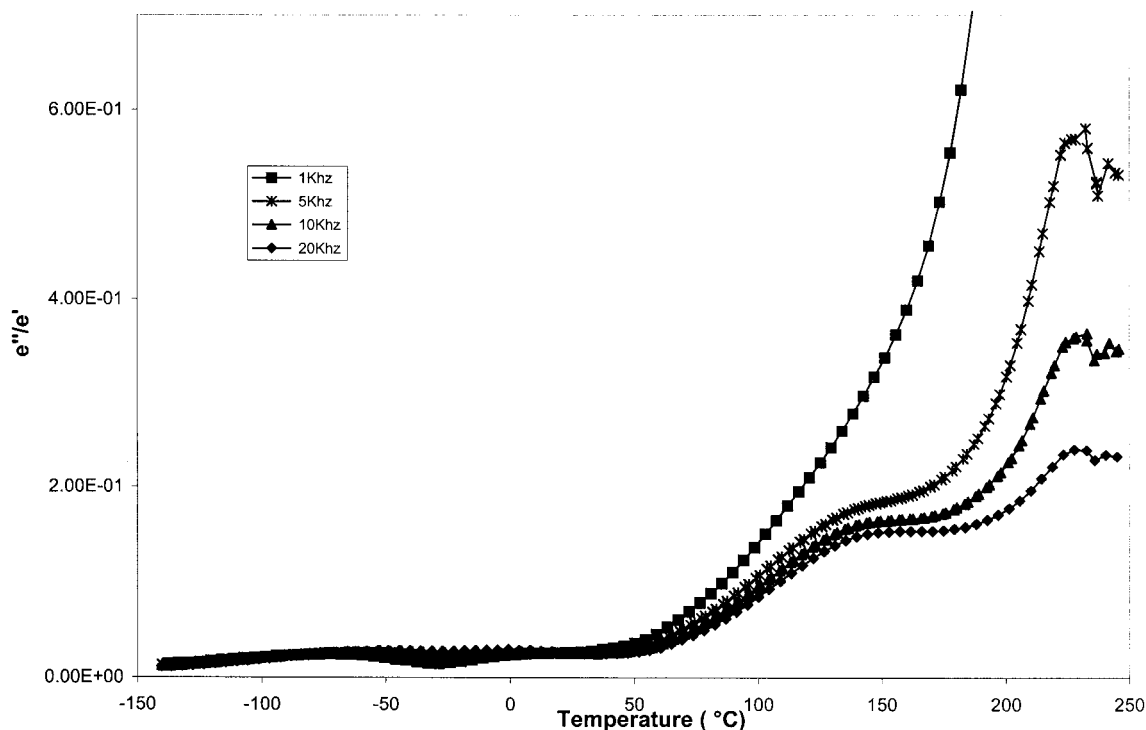


Figure 6 DEA $\tan \delta$ versus temperature for semi-IPNs with 41.03% PVP at frequencies of 1, 5, 10, and 20 kHz.

kHz relaxation curves. Such high values of DEA losses, shown in Figure 3, and M'' , shown in Figure 4, at low frequencies and high temperatures generally indicate the existence of ionic polarization in the PU network due to free charge motion within the material. The build-up of charges in the material and at the ends of conductivity paths leads to so-called conductivity relaxation and reflects the distribution of the conductivity relaxation times.^{21,22}

For the PVP sample, in a similar way to the mechanical relaxation behavior measured by DMA the DEA spectra also showed three relaxation processes which could be assigned similarly to the DMA measurements of the β -relaxation and the α_T - and α_U -relaxations.

This is demonstrated in Figure 5(a,b), where the logarithm of the DEA $\tan \delta$ is plotted versus temperature and frequency. As for the mechanical measurements, the DEA relaxation spectra are also discussed in order of increasing temperature or decreasing frequency. At low temperatures ($-100 \div 0^\circ\text{C}$), as shown in Figure 5(a), a broad relaxation process, referred to as the β -relaxation process, was observed, which shifted to higher temperatures with increasing frequency. It was attributed to the local motion of the side groups of the main PVP chain in the glassy state.²³

As the temperature increased a second relaxation process, looking like a shoulder, appeared in the temperature range of $50\text{--}110^\circ\text{C}$ [Fig. 5(b)] The temperature position of this shoulder was frequency depen-

dent and was related to the first T_{g1} of PVP observed in DSC and DMA.

In the temperature range $+125\text{--}+175^\circ\text{C}$, a frequency-dependent third relaxation was observed on the DEA spectra [Fig. 5(b)]. This phenomena was related to the second T_{g2} of PVP.

Now that assignments to molecular motions of the relaxation processes of the PU and PVP homopolymers have been done, we examine the DEA behaviour of one semi-IPN sample. The 41.03% PVP semi-IPN sample showed four DEA relaxation processes as shown in Figure 6, which represented the evolution of $\log \tan \delta$ versus temperature. In the low-temperature domain (-100 to -30°C), there was a broad relaxation peak that correlates in fact with both β -relaxation processes in the PU and PVP phases of the semi-IPN, which more or less overlapped in this range of temperatures. The next loss peak observed in the temperature range (-30 to 25°C) was assigned to the α -relaxation of the PU phase of the semi-IPN. At higher temperatures ($75^\circ\text{--}150^\circ\text{C}$), a very intensive and broad relaxation was observed, which had to be a combination of the conductivity relaxation of the PU network and the α_T -relaxation process of PVP. As the temperature increased ($175\text{--}220^\circ\text{C}$), the next relaxation process appeared, shifting also to higher temperatures with increasing frequency. This was attributed to the α_U -relaxation process of PVP.

To examine the evolution of the DEA behavior of the semi-IPNs with their composition, Figure 7 presents the variation of $\log (\tan \delta)$ of a few of the semi-

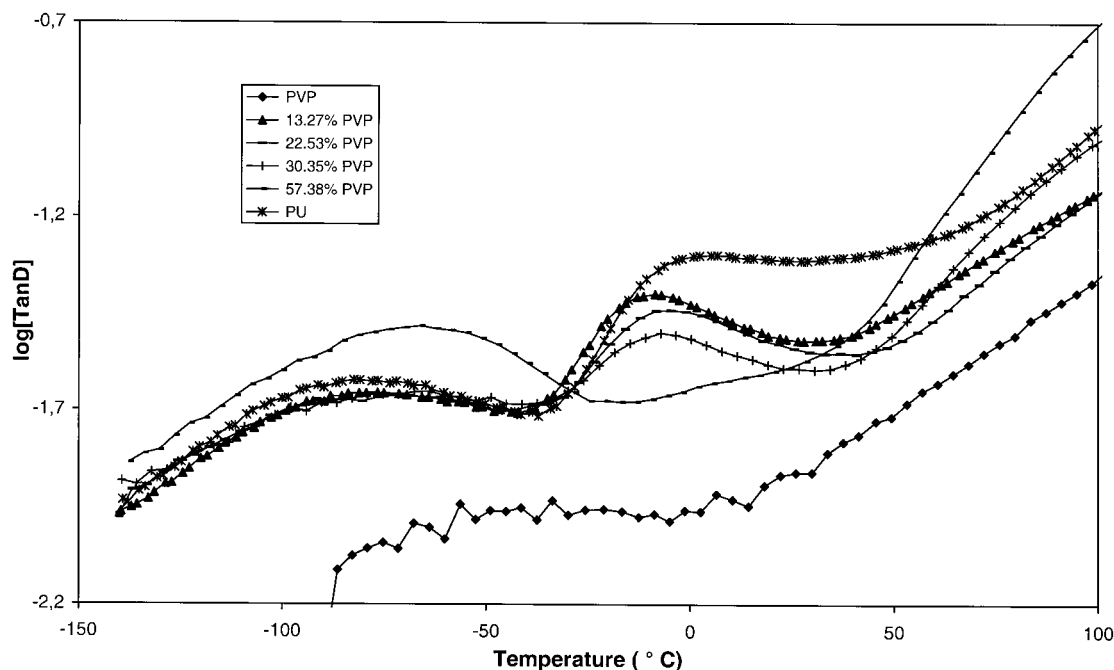


Figure 7 Temperature dependence of the logarithm of $\tan \delta$ at a frequency of 5 kHz for PVP, PU, and semi-IPNs with 13.27, 22.53, 30.35, and 57.38% PVP.

IPNs in the temperature range -150 to 100°C at 5 kHz. The position of DEA relaxation, which correlated with α -relaxation in the PU network (-25 to 25°C) was the same in all of the investigated semi-IPNs and in the pure PU. This was also in agreement with the corresponding data of the DSC measurements (Table I) and with the results of DMA. The magnitude of the relaxation process of the α -relaxation of PU decreased with increasing PVP in the semi-IPNs. This relaxation was associated with the glass transition of PU. The evolution of the amplitude of the relaxation was sensitive to the number of PU chain segments involved in the relaxation, which changed as the proportion of PU–PVP content changed.

Due to an overlooping of the dielectric processes and the conduction effect, it was difficult to analyze the $\tan \delta$ spectra at high temperatures.

To obtain a better analysis of these relaxation processes in the domain of high temperatures we represent in Figure 8 the variations of M'' , as previously done in Figure 4 for pure PU, versus temperature for the different semi-IPNs.

The maximum conductivity relaxation of PU (at 100 Hz) was observed at 60°C . In the semi-IPNs, this maximum conductivity relaxation of PU shifted to higher temperatures with increasing PVP in the semi-IPNs up to 22.53%. This very intensive peak of the conductivity relaxation of PU in the semi-IPNs masked the α_T - and α_U -relaxations of PVP in the systems. In the semi-IPNs with concentrations of PVP from 30.35 to 57.38%, we observed only α_U -relaxations of PVP in a temperature

range of 70 – 200°C . This α_U -relaxation of PVP in the semi-IPNs shifted to low temperatures in comparison with individual PVP (Fig. 8).

So, the sensitivity of the α_T -relaxation process to the conductivity phenomena of the PU was obvious below 41.03% PVP content in the semi-IPNs. Above this composition, it was clear that 57.38% PVP semi-IPNs had distinct α_T and α_U -relaxations with respective amplitudes of relaxation that were in balance compared to the two relaxations of pure PVP. The DEA phenomena were very sensitive to the type of interaction in such materials as far as such interactions change, whether it was pure PVP or PVP already mixed with 42.62% of PU. It was possible to explain the upper part of the α_U relaxation, even it was rather difficult to show that it was due to the conduction of the systems.

It was possible to analyze the evolution of the permittivity values with temperature (Fig 9). From -150 to 50°C , the two successive steps in the permittivity behavior that correspond to the β -relaxation of PU and PVP and to the α -relaxation of PU were observed. Then, we observed a large increase of the permittivity at 50 – 100°C for pure PU, which could be connected with its conductivity relaxation.²⁴ When the amount of PU decreased in the semi-IPNs, at 7.05–22.53% PVP, the dielectric increment of the relaxation in this region became lower and was associated to the effect of concentration of PU in the samples. Starting from 150°C , all of the semi-IPN samples presented a new rise in permit-

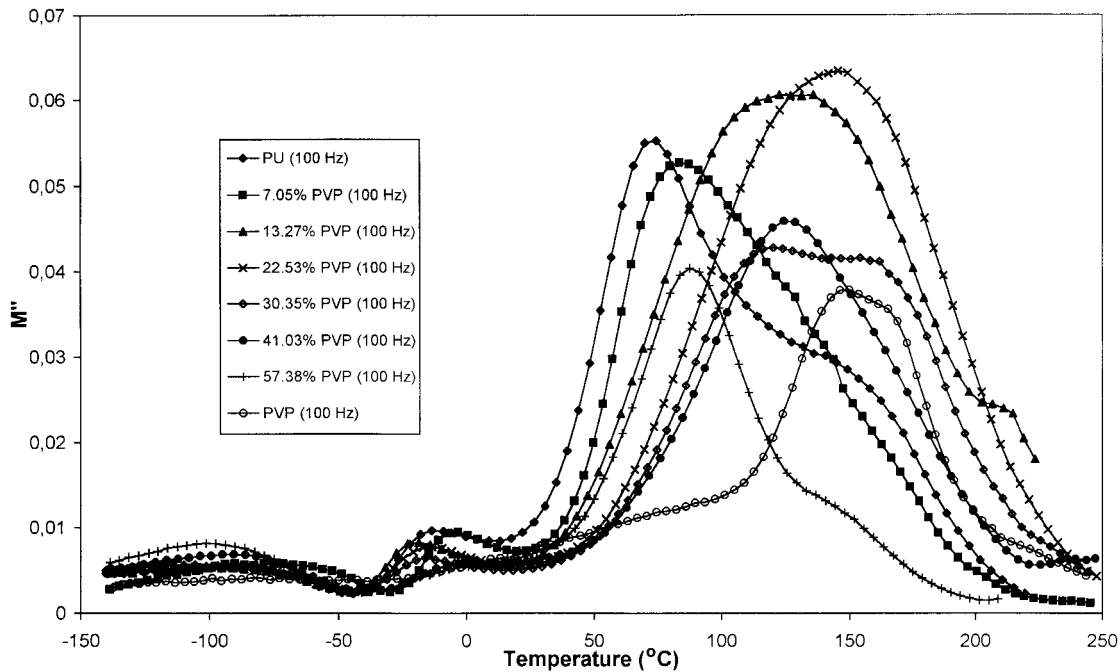


Figure 8 Temperature dependence of M'' at a frequency of 10^2 Hz for PU, PVP, and semi-IPNs with 7.05, 13.27, 22.53, 30.35, 41.03, and 57.38% PVP.

tivity with a stabilization around 200°C , with the exception of the 57.38% PVP in the semi-IPNs. This could be evidence of the second α_u -relaxation related to the high T_g of PVP.

With regard to the β - and α -relaxation processes related to local and long-range motion, it was not

possible to draw the relaxation maps of the β - and α -relaxation processes of semi-IPNs due to the relatively narrow range of frequencies of these studies by the DEA DuPont analyser and due to the evident overlooping of these processes without deconvolution of the complex DEA spectra.

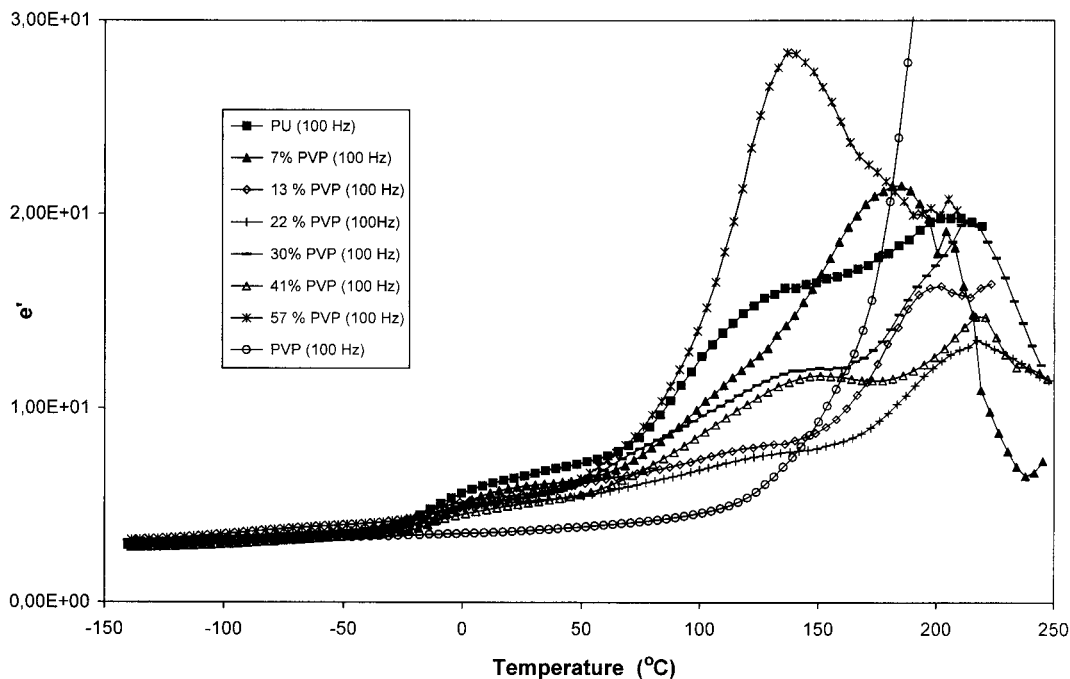


Figure 9 Permittivity versus temperature at a frequency of 10^2 Hz for PU, PVP, and semi-IPNs with 7.05, 13.27, 22.53, 30.35, 41.03, and 57.38% PVP.

CONCLUSIONS

The thermal and dynamic mechanical behavior and the dielectric properties of semi-IPNs based on crosslinked PU and PVP were investigated.

Thermal analysis showed the T_g of PU but also two T_g values for PVP. As this point was not clear in literature until now, this work is important as DMA and DEA relaxation spectra confirmed these two T_g values.

The DMA data revealed a pronounced change in the viscoelastic properties of semi-IPNs with different amounts of PVP in the samples. The semi-IPNs had three distinct maximum $\tan \delta$ related to the thermal transitions of the two polymer constituents observed in their glass temperature domains. The temperature position of the PU maximum $\tan \delta$ was invariable with different compositions of IPNs, but the high amplitude of PU relaxation became lower in semi-IPNs with increasing PVP in the systems. The highest maximum $\tan \delta$ of PVP for α_u -relaxation was shifted to a lower temperature, and its amplitude decreased when the amount of PVP in the semi-IPNs became lower.

The second relaxation of PVP (α_f -relaxation) for low contents of PVP in IPNs was rather well defined. This was no more the case when the PVP amount increased as the α_f -relaxation transformed only in a shoulder to the main α_u -relaxation.

By means of DEA relaxation spectroscopy, six relaxation processes were observed: a secondary β -relaxation due to PU, a secondary β -relaxation due to PVP, an α -relaxation due to the glass-rubber transition of PU, two α -relaxations due to the glass-rubber transitions of PVP, and a conductivity relaxation due to the space charge polarization of PU. The temperature position of the α -relaxation of PU was invariable in the semi-IPNs. However, the α_u -relaxation process of PVP shifted to higher temperatures with increasing PVP content in the semi-IPNs. So, such results reflected perfectly what was shown in DMA.

We concluded that the investigated semi-IPNs were two-phase systems, but the phase separation was incomplete in these materials. The separation into two phases occurred. One phase was the PU phase not influenced by PVP component. On the contrary, the phase based on PVP in the semi-IPN was not a pure PVP phase but a solution of component 1 into component 2 of the semi-IPNs.

This study showed the complementarity of DEA and DMA spectroscopy for studying semi-IPNs with the molecular mobility as a probe for structure. Each experimental method has shed light on different as-

pects of the molecular motions that are under investigation.

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