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ESR-spin labelling study of semi-interpenetrating networks and polymer mixtures based on functionalized polyurethanes and polymethacrylates

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Abstract

Semi-interpenetrating polymer networks, SIPNs, and polymer mixtures (1:1 mass ratio) based on segmented polyester polyurethane, PU, with carboxylic groups and methacrylic copolymer, PM, with tertiary amine groups were prepared. Electron spin resonance, ESR, spin label method was used to study the effect of functional groups concentration on the segmental motion, motional transitions and phase separation. The concentration of functional groups varied from 0 to 0.45 mmol g^{-1}. From the temperature dependent composite ESR spectra of PU labelled component motional heterogeneity was deduced. Restriction of segmental motion of PU segments in the PU/PM mixtures increases with the augmentation of functional groups content due to the additional noncovalent interactions. The critical concentration (0.35 mmol g^{-1}) above which the motional restriction decreases is observed. The effect of functional groups is discussed in terms of the change of local packing density. According to the fractions of the slow component and temperatures of motional transitions SIPNs reveal better interpenetration and interactions of both polymer components. Additional functional groups contribute to a very strong influence of restricted PM chains on the PU hard segments.
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Keywords: Semi-interpenetrating polymer networks; Polyurethanes; Polymethacrylates; ESR; Motional heterogeneity

1. Introduction

Interpenetrating polymer networks, IPNs, and semi-interpenetrating polymer networks, SIPNs, based on segmented polyurethanes represent a class of polymeric systems with interesting and versatile mechanical and chemical properties. Compatibilization of polymer components in SIPNs changes polymer morphology due to the crosslinking and grafting and introduces considerable enhancement in mechanical properties [1–4]. However, some degree of phase separation due to the limited compatibility of the polymer components is observed in most SIPNs. In order to generate better compatibilization or disruption of domains of segmented PU and PM copolymer additional reactive functional groups are incorporated into the backbone of both polymer components [5]. Due to the interactions between polymer segments of two polymers the nature of molecular

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motion will be changed. Additional interactions and segmental composition introduce heterogeneity of molecular motion in the vicinity of glass transition temperature, T_g These multiple segmental motions improve the compatibility and mechanical properties, namely damping properties when acrylic esters were introduced as comonomer system [3].

Network morphology has been widely explored by a number of methods such as optical microscopy, scanning electron microscopy, transmission electron microscopy, wide angle X-ray scattering, small angle X-ray scattering, small angle neutron scattering and solid state nuclear magnetic resonance [1]. However, the amount of papers addressing their local segmental motions or motional heterogeneity remains limited [6–8]. The electron spin resonance, ESR, spin label method is chosen to gain an insight into the segmental motion and degree of phase separation [9]. The nitroxide molecule covalently attached to the chains as a label reflects local molecular motion of the chain segments in the vicinity of the label. ESR spectra of nitroxide radicals are sensitive to the label environment and if the rates of segmental motions are different complex spectra appear. Thus, the spin label method enables to explore motional and structural heterogeneities in multicomponent polymer systems at the segmental level. In our previous paper we have reported motional heterogeneity and phase separation of functionalized polyester polyurethanes [10].

In the present paper we study semi-interpenetrating networks and mixtures of the polyurethane, PU, and polymethacrylate, PM, component. The miscibility of PU and PM component was additionally enhanced by introduction of complementary functional groups: carboxylic groups in the hard segments of PU and tertiary amine groups in PM copolymer. The extent of miscibility of the similar functionalized SIPNs has already been reported and some structure–property relationships established [5]. It remains to find out how the local dynamics of the labelled PU segments in the presence of PM chains is changed depending on functional groups concentration or additional segmental interactions and how these interactions affect phase separation. The information about the change of motional heterogeneity at temperatures near the glass transition temperature may be used to understand how these local motions reflect mechanical performance of the network. Motional heterogeneity and motional transitions were correlated with the DSC measurements.

2. Experimental

2.1. Materials

Polyester polyurethanes (PU) with carboxylic functional groups in the hard segments of polymer chain were prepared from isophoronediisocyanate (IPDI), polycaprolactone (PCL) [average molecular mass, $M = 2000$], 1,4-butanediol (BD), and 2,2′-bis-(hydroxymethyl) propionic acid (DMPA) according to the procedure described in the previous articles [5,10]. The hard segments of the PU were labelled with nitroxide radical 2,2,6,6-tetramethyl-4-aminopiperidin-1-yloxyl, TAMINE. Methacrylic (PM) components with tertiary amine functional groups were synthesized from methyl methacrylate, *N*,*N*-dimethylaminoethyl methacrylate and hydroxylethyl methacrylate [5]. The concentration of functional groups in both polymers varied from 0 to 0.45 mmol g^{-1}. Functional group concentration and the corresponding molecular mass of each polymer component are shown in Table 1.

Labelled PUs and labelled hard PU were mixed with the corresponding PMs prepolymers of the same functional groups concentration in 1:1 mass ratio in 2-butanone and stirred 24 h. After the solvent had slowly evaporated off, the mixtures were further annealed in a vacuum at 363 K for 48 h.

In the preparation of SIPNs an equal mass quantities of both prepolymers were dissolved in 2-butanone. After 24 h of stirring 10 mass% solution of the crosslinking agent DDA in 2-butanone was admixed in a 100% excess to the calculated amounts of OH groups in both components [5]. After 15 min of mixing the films were obtained by casting 2-butanone solution of the polymer mixture on heated (333 K) glass plates. The crosslinking was performed in a vacuum for 4 h at 363 K and 16 h at 313 K (Scheme 1). Prior to ESR measurements polymer films were annealed in vacuum for 48 h at 363 K.

SIPNs with labelled PU and various functional group concentrations are designated SIPN-0, SIPN-25, SIPN-35, SIPN-45, while PU/PM indicates a mixture with labelled PU component.

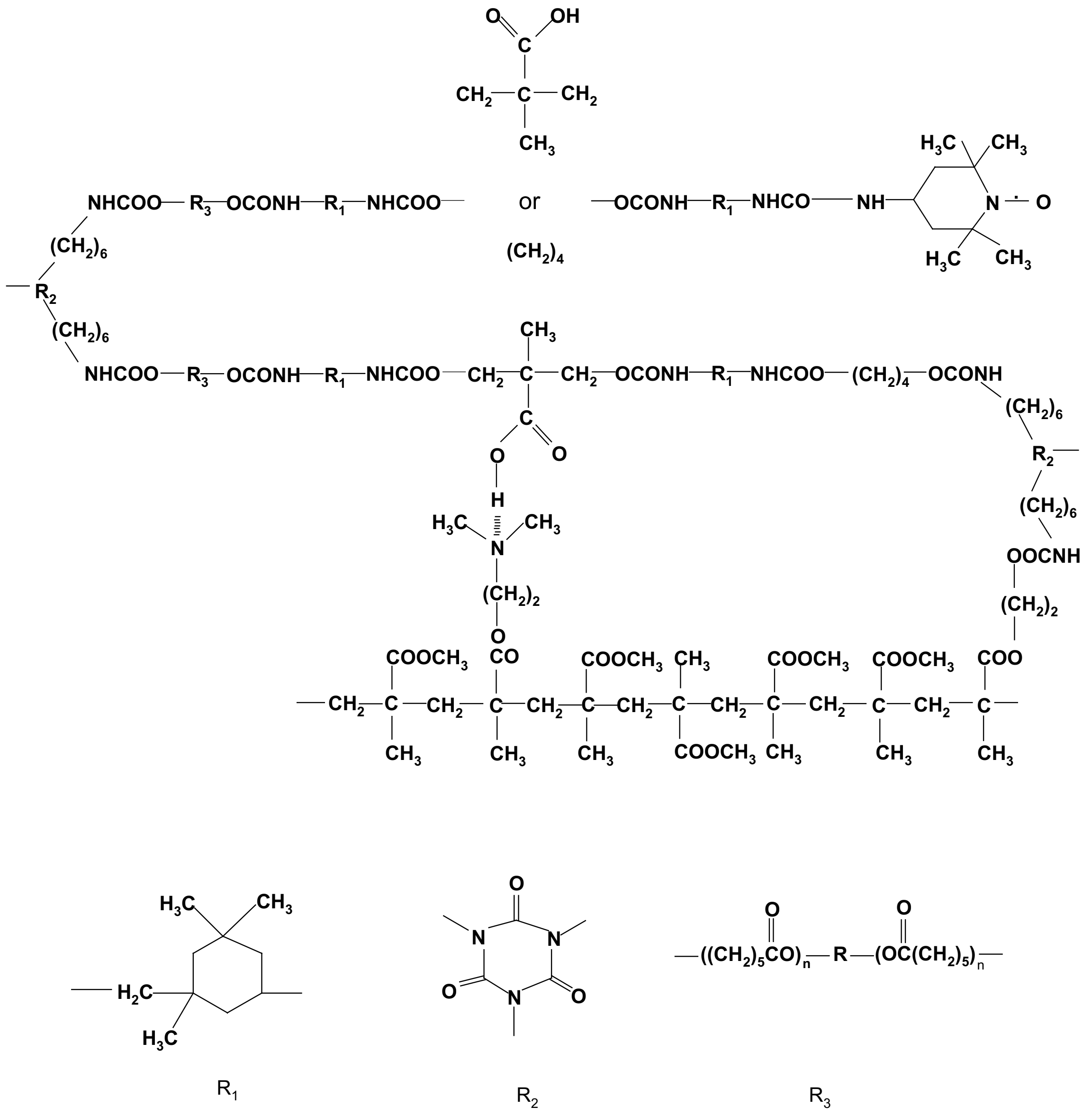
2.2. Methods

The ESR spectra were recorded on a Varian E-109 X-band spectrometer operating at 9.76 GHz with 100 kHz modulation. The spectra were collected with the following parameters: 16 mT sweep width, microwave power less than 5 mW, modulation amplitude 0.1 mT, scanning time 25 s, 5–50 scans (depending on the signal to noise ratio) and 1000 points. The temperature was controlled using a variable temperature unit Bruker ER 4111 VT with a flow of cold nitrogen gas. The samples were allowed to equilibrate about 15 min after approaching the corresponding temperature.

The simulation of the complex experimental two component spectra is made with a set of experimental narrow and broad components covering the wide range of rotational correlation times. The analysis of a single component fast motion of PU with end labelled hard segments spectra shows that the lineshape of narrow

Table 1
Characteristics of the mixtures and networks

Sample	Concentration of functional groups (mmol g^{-1})	M_n of PU prepolymer	M_n of PM prepolymer
SIPN-0, PU/PM-0	0.00	80,500	11,200
SIPN-25, PU/PM-25	0.25	13,400	11,400
SIPN-35, PU/PM-35	0.35	14,500	10,500
SIPN-45, PU/PM-45	0.45	10,000	10,700



Scheme 1.

spectral component in the complex spectra originates form the anisotropic reorientation of spin labels. The broad components obtained by subtraction of experimental PU narrow components from the complex spectra of mixtures and SIPNs also exhibit anisotropic motion. From the set of calculated spectra obtained by combining all pairs of motional components the spectra giving the best fit (with the deviation of less than 3%) is used for determination of fractions in the experimental spectra. The complete ESR lineshape analysis would require a number of additional parameters due to a large number of possible intra and intermolecular interactions, and that is not a subject of the present paper.

DSC measurements were conducted on a Perkin–Elmer Pyris 1 calorimeter in the temperature range from 213 to 373 K at a heating rate of 20 K min^{-1}. The second heating cycle was used for the calculation of glass transition temperatures.

3. Results and discussion

3.1. Motional heterogeneity of PU/PM mixtures

Compatibilization of the two functionalized polymers was examined through molecular motion and local heterogeneity of spin labelled PU hard segments. ESR spectra of spin labels in polymer mixtures with different functional groups concentration were measured in the temperature range from 173 to 393 K at intervals of 5 K. Fig. 1a presents selected spectra of the labelled PU/PM mixture without additional functional groups. At low temperatures the ESR spectra are characteristic for the slow motion regime with outer maxima separation, $2A_{zz}$, of about 6.8 mT. Above 323 K the outer maxima shifts inwards giving rise to a relatively narrow three-line spectrum indicating a transition from slow to fast motion at the labelled PU chain ends. The ESR spectra of PU/PM mixtures with additional functional groups in certain temperature interval display a complex structure. As an example PU/PM mixture (Fig. 1b) with 0.45 mmol g^{-1} of functional groups shows two component ESR spectra corresponding to the fast and slow motion of spin label. In other words labelled PU ends are placed in motionally different environments in the polymer mixture. Similar ESR spectra are observed in the pure PU functionalized prepolymer [10]. Motional transitions of PU/PM mixtures are derived from the change of $2A_{zz}$ with temperature (Fig. 2). The inflection point of the sigmoidal curve defines an empirical parameter $T_{5\,\mathrm{mT}}$. Since the spin probe motion is coupled with thermally activated segmental mobility of polymer chains $T_{5\,\mathrm{mT}}$ is related to the matrix glass transition temperature, T_g. Generally, $T_{5\,\mathrm{mT}}$ values are higher than those of T_g as shown and discussed in the literature [11,12]. In the present analysis it was important to determine the difference in mobility monitored by the functional groups interaction in polymer network. The $T_{5\,\mathrm{mT}}$ shifts are used to compare motional restrictions. In the case of two-component spectra we define the

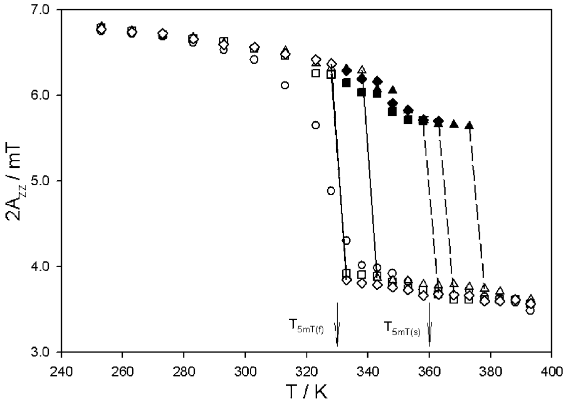


Fig. 2. The temperature dependence of the outer maxima separation, $2A_{zz}$ of PU/PM mixtures of spin labelled PU with various functional group concentration: PU/PM-0 (○), PU/PM-25 (□), PU/PM-35 (△) and PU/PM-45 (◇). The temperature at which the $2A_{zz}$ of the fast and slow component is 5 mT (indicated by arrows and marked as $T_{5\,\mathrm{mT(f)}}$ and $T_{5\,\mathrm{mT(s)}}$). The full points mark the presence of the slow along with the fast component.

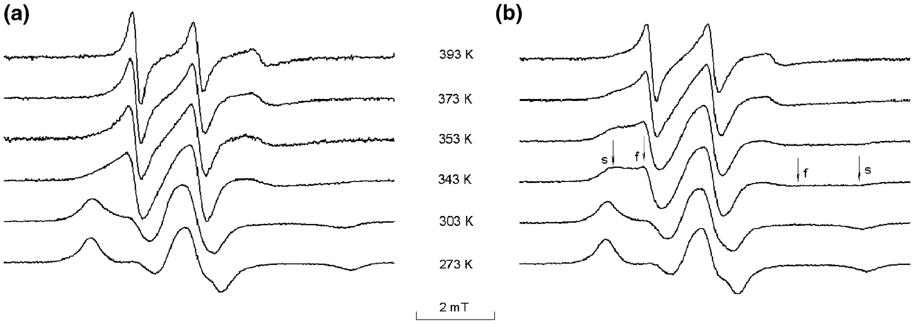


Fig. 1. Temperature variation of the ESR spectra of PU/PM mixture without additional functional groups (a) and with 0.45 mmol g^{-1} of functional groups (b). Fast (f) and slow (s) components are indicated by arrows.

appearance of the fast component as $T_{5\,\mathrm{mT(f)}}$ and the disappearance of the slow component (second transition) as $T_{5\,\mathrm{mT(s)}}$. Those temperatures depend on the functional group concentration and are 10–15 K lower compared to the corresponding temperatures of the pure PU components [10] (Table 2). The origin of the fast motion in the mixture of functionalized PU and PM components may either be a consequence of the influence of PU soft segments [10] or the free volume created at the interphase of phase separated mixtures in which the labelled chain ends are placed [13–16]. In order to analyse the origin of the fast motion in the complex ESR spectra the hard segments of functionalized PU were mixed with the corresponding PM components. The ESR spectra of the mixtures do not show two component spectra in the experimentally accessible temperature range. Only a slight narrowing of the $2A_{zz}$ value is observed at higher temperatures (above 340 K). As an example Fig. 3 displays the ESR spectra of PU hard segments/PM mixture with 0.45 mmol g^{-1} of functional groups. Therefore, the fast motion in the complex spectra is ascribed to the influence of flexible PU segments. Two-phase morphology of segmented polyester polyurethanes has been discussed in terms of soft and hard segments. Though DSC measurements display a single glass transition temperature (Table 3) indicating miscibility of hard and soft segments, ^{2}H NMR and ESR confirm motional heterogeneity on the segmental scale [8,17]. The question arises how those motions are influenced by the PM components. Two spectral parameters were taken into consideration. First, the temperature at which the fast component appears in the mixtures of functionalized components in comparison with the pure components. The second parameter is the ratio of fast and slow ESR component (Table 4). The intensity of fast motion in the mixtures increases at the same temperatures as compared to the corresponding PU pure components [10]. Obviously, a fraction of hard segments attaining fast motion in the presence of PM component is higher. Since the PM segments are well bellow the T_g at temperatures of measurements increased molecular motion should be looked for in the change of domain structure of the PU hard segments. Functionalized PM component in the mixture due to the intermolecular interactions

Table 2
Spectral parameters of PU/PM mixtures and SIPNs

Sample	$T_{5\,\mathrm{mT(f)}}$ (K)	$T_{5\,\mathrm{mT(s)}}$ (K)	$\tau_R \times 10^{9}$[a] (s)
PU/PM-0	–	325	2.1
PU/PM-25	330	360	2.9
PU/PM-35	340	376	3.3
PU/PM-45	330	366	2.8
SIPN-0	–	346	–
SIPN-25	350	–	–
SIPN-35	360	–	–
SIPN-45	355	–	–

[a] Determined at 393 K.

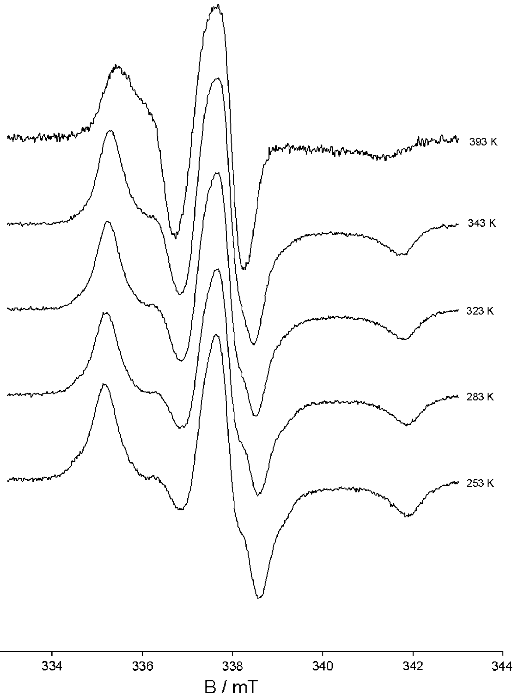


Fig. 3. Temperature variations of the ESR spectra of PU hard segment/PM mixtures with 0.45 mmol g^{-1} of functional groups.

Table 3
Glass transition temperatures of pure PU and PM prepolymers (T_{g1}), PU and PM in mixtures (T_{g2}) and SIPNs (T_{g3}) determined by DSC

Concentration of functional groups (mmol g^{-1})	T_{g1} (K)		T_{g2} (K)		T_{g3} (K)	
	PU[a]	PM	PU	PM	PU	PM
0.00	254	373	253	366	253	378
0.25	265	368	270	354	277	369
0.35	269	367	285	365		360
0.45	273	366	297	356		330

The accuracy of T_g determination is ±5 K.

[a] From Ref. [10].

Table 4
Fractions of the ESR slow component of PU/PM mixtures

Sample	343 K	348 K	353 K	358 K	363 K
PU/PM-0	–	–	–	–	–
PU/PM-25	0.90	0.77	0.65	0.56	0.52
PU/PM-35	0.97	0.91	0.80	0.75	0.60
PU/PM-45	0.91	0.86	0.76	0.70	0.55

disrupts a hard domain structure of PU component enabling thus a number of hard segments to be plasticized by the soft segments. The effect of increased motion of hard segments of polyether polyurethanes in the mixture with other polymers has also been observed by DMA method [18] and explained by the disruption of hard segment interactions [19]. Dispersions of PU hard segments in the PM matrix leads to the formation of smaller domains. Thus, the decreased values of temperatures of motional transitions, $T_{5\,\mathrm{mT(f)}}$, of the plasticized PU hard component is expected. However, the increased values of the glass to rubber transition, T_g of functionalized PU in the mixtures indicate better interaction or a higher degree of mixing of the two components. In the case of functionalized polymers the miscibility is improved trough specific interactions between the mixed constituents. Namely hydrogen bonding between the carboxylic and tertiary amine groups incorporated into the PU and PM component introduces structural changes in the matrix [20]. Steric effects of DMAEM introduced into PM chains at higher functional group concentrations will also influence local chain ordering. As a consequence local free volume and local chain mobility will also change. With an increase of functional group concentration the temperatures of fast motion appearance are shifted to higher values and a fraction of slow molecular motion is increasing. However, both values are smaller in comparison with the pure PU polymer. With a further increase of functional group concentration a fraction of slow motion begins to decrease. The same is valid for $T_{5\,\mathrm{mT(f)}}$ (Table 2). Furthermore, the rotational correlation times calculated from the ESR spectra [21] at 393 K, where only fast motion is present, show the same behaviour; the rotation is reduced as functional groups are introduced and with further increase of functional group concentration τ_R is faster. Additional hydrogen bonding and possible heterocontacts between the polymer components bring more PU hard chains in a closer contact with the soft segments and drive the system to better miscibility. The change in local structure as a consequence of hydrogen bonding in binary blends and the existence of a critical level of hydrogen bonds has been observed for the first time using annihilation spectroscopy [20]. It should be mentioned that the trend of motional changes with increasing functional group concentrations in PU/PM mixtures is the same as in the pure PU components [10]. Therefore, the changes of ESR spectral parameters can be explained with the interactions between the PM and PU segments and hard and soft PU segments due to the sterical and hydrogen bonding effects.

3.2. Motional heterogeneity of semi-interpenetrating network with labelled PU component

Motional heterogeneity and the extent of interactions in SIPNs with labelled PU component are compared with polymer mixtures of the same compositions. ESR spectra of SIPN without incorporated carboxylic groups are measured over the temperature interval 170–400 K (Fig. 4a). The variation of $2A_{zz}$ at temperatures lower than ~300 K is very small indicating that polymer dynamics does not change markedly in this temperature interval. Above 350 K a characteristic transition from the slow to fast motion is observed (Figs. 4a and 5). This sigmoidal transition of the $2A_{zz}$ vs. temperature is similar to that in PU/PM mixture. However, the temperature of characteristic sigmoidal transition $T_{5\,\mathrm{mT}}$ is shifted to higher temperature in case of SIPNs (Table 2). Covalent bonding between the polymer components in SIPNs is expected to restrict segmental motional dynamic of PU chains. In addition carboxylic groups incorporated into the PU hard segments and tertiary amine groups into the PM chains increase the possibility of complex interactions in the network. Those complex interactions influence the change of local free volume and segmental motion, which is reflected in the shapes of temperature dependent ESR spectra. Above certain temperature in the intermediate regime of the rotational correlation times (10^{-10} s < τ_R < 10^{-8} s) composed spectra appear

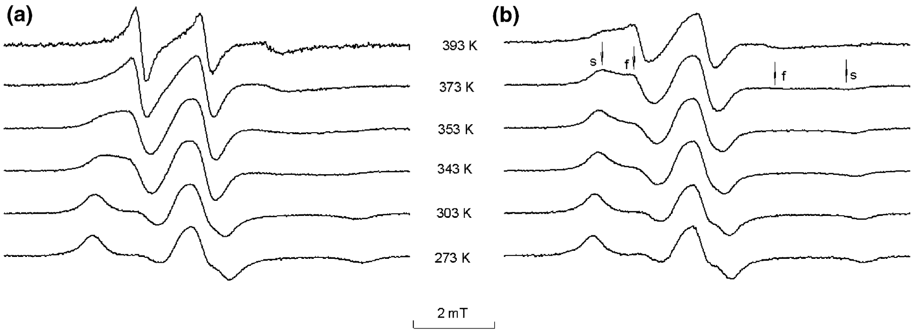


Fig. 4. Temperature variations of the ESR spectra of SIPNs with labelled PU component without additional functional groups (a) and with 0.45 mmol g^{-1} of functional groups (b). Fast (f) and slow (s) components are indicated by arrows.

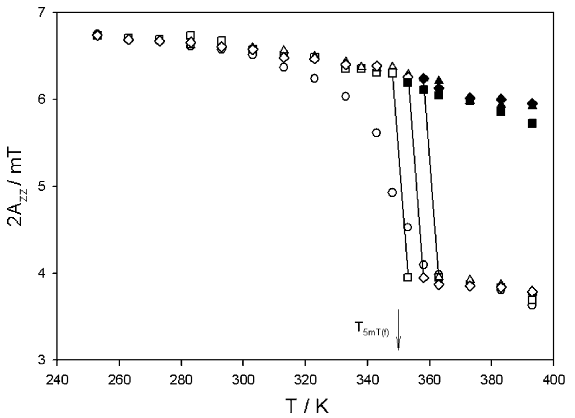


Fig. 5. The temperature dependence of the outer maxima separation, $2A_{zz}$ of SIPNs of spin labelled PU with various functional group concentration: SIPN-0 (○), SIPN-25 (□), SIPN-35 (△) and SIPN-45 (◇). The temperature at which the $2A_{zz}$ of the fast component is 5 mT is indicated by arrow and marked as $T_{5\,\mathrm{mT(f)}}$. The full points mark the presence of the slow along with the fast component.

indicating a portion of PU labelled segments placed in two motionally different environments. SIPN-45 is chosen to illustrate ESR complex spectra (Fig. 4b). The fast motion component of the labelled hard segment is explained by the plasticization of PU hard segment with PU soft segments. The remaining hard component corresponds to PU hard segments in motionally restricted regions of the network. Motional restriction except the covalent bonding is additionally caused by the intermolecular interactions of PU hard segments and PU and PM segments via functional groups. The temperature at which the fast motion appears is determined by the functional groups (Table 2) and has the highest value at 0.35 mmol g^{-1}. With further increase of functional group content $T_{5\,\mathrm{mT(f)}}$ is lowered. Similar behaviour is observed in the PU/PM mixtures and pure PU polymer [10]. However in SIPNs $T_{5\,\mathrm{mT(f)}}$ temperatures are shifted to higher values. It should be noted that the high fraction of slow component of ESR spectra is present up to ~400 K indicating highly restricted local segmental motion that is not the case in PU/PM mixtures. The presence of highly restricted motion of PU segments at higher temperatures may be explained by a very strong influence of restricted PM chains covalently attached and additionally bound by noncovalent bonds to PU chains. DSC measurements of SIPN-0 and SIPN-25 reveal the presence of two glass transitions. T_g values of the PU component in the network are increasing with the functional group concentration and are shifted toward higher temperatures as compared to the PU pure component. The T_g shifts are explained with the increased internetwork interactions and crosslinking, which contribute to better mixing of the two polymers. SIPNs with higher concentration of functional groups: SIPN-35 and SIPN-45 show a single broad glass transition (Table 3) indicating heterogeneous morphology [22]. Two motional environments of the same networks observed from the ESR spectra are the result of the spin label sensitivity to segmental motion on a length scale shorter than those responsible for the glass transition temperature. As already discussed in our previous papers the ESR method is able to detect a very small fraction of discrete fast local motions and the change of these motions with temperature [10,23].

It is known that the local distribution of fast motion and the extent of motional heterogeneity of polymer mixtures or SIPNs based on segmented polyurethanes determine mechanical properties such as modulus and damping properties [3]. The experimental complex spectra are analysed to determine a fraction of fast/slow motion. As discussed in our previous paper [10], the correlation times of extracted broad component are one order of magnitude faster compared to the slow components of the PU hard segments due to the influence of soft segments.

A fraction of fast motion is increasing with temperature as expected due to the free volume change. However, motional changes are modulated by the additional internetwork interactions introduced by functional groups. A fraction of slow or restricted motion is increasing with the functional group concentration (Table 5). There is a considerable increase of slow motion in SIPNs in comparison with the corresponding mixtures (Table 4). Restriction of molecular motion of PU segments in SIPNs is expected due to the crosslinking and/or grafting [2,3]. The fraction of plasticized PU segments in SIPNs is further lowered by additional intermolecular interactions of PU hard segments and PM segments. These results can be compared with similar systems in the literature [2,4]. Obviously, crosslinking and/or grafting has a profound influence on the segmental motion of PU chains in the network. Since the concentration of –OH groups in the methacrylic component is the same in all samples the number of bonding sites is equal irrespective of the additional functional groups. However, in the case of SIPN without functional groups molecular mass of PU component is larger as compared with the functionalized PU components. Thus is expected that SIPN-0 has considerably longer

Table 5
Fractions of the ESR slow component of SIPNs

Sample	353 K	363 K	373 K	383 K	393 K
SIPN-0	–	–	–	–	–
SIPN-25	0.99	0.95	0.92	0.70	0.55
SIPN-35	1.00	0.96	0.93	0.80	0.64
SIPN-45	0.98	0.97	0.95	0.90	0.85

sequences between the crosslinks, which are able to attain faster motion at lower temperatures. By comparing the results of polymer mixtures and SIPNs with labelled PU component (Tables 4 and 5) and SIPNs with labelled PM component [24] it can be concluded that the differences between the functionalized polymers are mainly determined by the specific interactions. It can be noted that the change of $T_{5\,\mathrm{mT(f)}}$ corresponding to the motion of plasticized PU hard segments in SIPNs depends on the fraction of functional groups (Table 2) and that the trend is the same as in pure PU (Table 2 in Ref. [10]). Some of chain ends of PU hard segments are not in the contact with the PM component and locally act as a pure PU component. However, a fraction of fast motion or plasticized PU segments depending on functional group concentration as already discussed differs from those in PU/PM mixtures and pure PU [10]. This behaviour is explained with considerable changes in chain packing due to crosslinking or grafting [2]. Disruption of the domain structure of PU hard segments due to the crosslinking and bonding of PU and PM chains enables further closer contact of the segments and consequently hydrogen bonding interactions. As a result better interaction and mixing of PU and PM chains is achieved. Better mixing is also seen in the DSC results (Table 3). Increased interactions between the PU hard segments and PM chains lower a fraction of plasticized PU segments that is easily explored by the ESR measurements. Furthermore, selective spin labelling of one component enables to observe separately motional and structural behaviour of one component in the presence of the other component.

4. Conclusions

The ESR data report how the complementary functional groups in segmented polyester polyurethane (PU) and polymethacrylate (PM) prepolymers influence motional heterogeneity and phase separation in their SIPNs and mixtures. Nitroxide molecule attached to the end of hard segments of PU prepolymer reveals different motional behaviour in the presence of PM chains as compared to the pure PU prepolymer. Composite ESR spectra with fast and slow component reveal the presence of two motionally different environments in both SIPNs and mixtures. The temperature region of the motional heterogeneity depends on the functional groups concentration. Analysis of the two component ESR spectra of PU/PM mixtures has shown an increased fast motion component of the PU segments in the presence of PM chains. The shift of motional transitions ($T_{5\,\mathrm{mT(f)}}$) indicates better interaction of functionalized components and a formation of smaller domains. Increased interactions or miscibility of PU hard segments and PM segments is confirmed by the higher T_g values of PU component in polymer mixtures. Critical functional groups concentration is also observed in PU/PM mixtures. Restricted motion is increasing due to the additional hydrogen bond interactions up to 0.35 mmol g^{-1}. Further introduction of functional groups increases polymer chain mobility due to the change of local packing. According to the $T_{5\,\mathrm{mT(f)}}$ shift to higher temperatures and the increased amount of slow motion component PU hard segments in the SIPNs reveal better interpenetration and interaction of polymer chains. Contrary to the PU/PM mixtures restricted motion increases linearly with the functional groups concentration. This effect is explained with the very strong influence of restricted PM chains covalently attached and hydrogen bonded to PU chains. The T_g values also confirm better interpenetration of the PU and PM chains in the SIPNs with an increase of functional groups content.

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