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Motional heterogeneity and phase separation of semi-interpenetrating networks and mixtures based on functionalised polyurethane and polymethacrylate prepolymers

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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 studied by the electron spin resonance (ESR) spin label method. The concentration of functional groups varied from 0 to 0.45 mmol g^{-1} in both prepolymers. The ESR spectra of spin labelled PM component were used to characterise the heterogeneity of segmental motion and transitions due to the additional polymer interactions imposed by complementary functional groups. The results were deduced from the temperature dependent ESR spectra. Two component spectra reflect the effect of PU chains on segmental motion of the PM component below the macroscopic glass transition temperature, T_g. The ratio of the fast and slow component was related to the complex polymer–polymer interaction or extent of miscibility. Restrictions of segmental motion of PM chains increase with functional groups concentration and above certain concentration (0.25 mmol g^{-1}) PM segments in the network assess faster motion suggesting a change in the local packing density and domain structure. An increased miscibility and disorganisation of the ordered domains are confirmed by the loss of spherulitic morphology and crystallinity at higher functional groups concentration. PU/PM mixtures reveal similar motional behaviour as SIPNs of the same composition. However, the differences in the fractional amount of fast and slow motions confirm better interpenetration and interaction of the two polymers in the SIPNs. The results of motional heterogeneity and polymer interactions were complemented with the T_gs.

Keywords: Functionalized polyurethane–polymethacrylate semi-interpenetrating networks; Heterogeneity; ESR

1. Introduction

Interpenetrating polymer networks, IPNs, and semi-interpenetrating polymer networks, SIPNs, based on polyurethanes offer a route for preparation of versatile materials with wide spectrum of properties [1]. The fundamental phenomena associated with the IPNs is the phase separation during the preparation. Many factors determine the phase separation and the properties of IPNs: the method of preparation, prepolymer miscibility, composition, chain structure, crosslinking density, domain size and crystallinity. Interpenetrating polymerisation is a way of blending two polymers where at least one of the polymers is crosslinked in the presence of another to produce a mixture of fine morphology [2,3].

In order to improve polymer miscibility by noncovalent interactions additional functional groups are incorporated in the backbone of constituent polymers [4–8]. Additional interactions influence the change of morphology and consequently mechanical and thermal properties [4,5]. Micro or nanoheterogeneous morphology of IPNs and SIPNs as a consequence of incomplete mixing is reflected in the broad glass transition. Differences of packing density within domains and local composition allow heterogeneity of segmental motions around glass transition temperature, T_g. Those multiple segmental motions can explain engineering performance of the material, namely mechanical

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damping properties [9,10]. Therefore the analysis of local segmental molecular motion could further contribute to the understanding of mechanical properties.

ESR spectroscopy of nitroxide radicals as spin labels or probes is a method that can offer an insight into the molecular motion and degree of phase separation [11–15]. The method is based on the sensitivity of the ESR line shapes to the local environment influenced by chain structure, molecular packing, ordering and polarity on a segmental level. Nitroxide radical covalently linked to the backbone of the polymer (a label) as molecular reporter reflects any change in segmental motion. Temperature dependent spectra are used to characterise motional dynamics. The appearance of the composite ESR spectra that evolve in a certain temperature range confirms the presence of more than one phase. Determination of the extent of motionally separated phases and their temperature dependence gives support for the interpretation and understanding of the polymer miscibility.

In our previous papers we reported on the molecular motion of mixtures and SIPNs of functionalised polyether polyurethane and polymethacrylate studied by using spin probe method and/or spin labelled polymetacrylate component [13,14]. Present study explores the extent of miscibility of SIPNs and polymer mixtures of segmented polyester polyurethane (PU) and methacrylic copolymer (PM). PUs with polyester soft segments exhibit improved miscibility of PU hard and soft segments [15] and, in addition, they contribute to the miscibility of PU and PM components as well [5]. Polymer interactions were enhanced by introduction of complementary functional groups; carboxylic groups in the hard segments of PU and tertiary amine groups in PM copolymer. The miscibility of functionalised SIPNs has already been reported and some structure-property relationship established [5]. In order to clarify polymer interactions in rather complex PU based networks at the segmental level we have used labelled PM chain to explore PU–PM interactions depending on the functional groups concentration. Information will be deduced from segmental motions and motional heterogeneity at temperatures close to the glass transition temperature. SIPNs are compared with the PU/PM mixtures of the same composition. Parallel observations were also carried out by differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD) and optical microscopy.

2. Experimental

2.1. Materials

2.1.1. PU prepolymers

The polyester polyurethane, PU, component with carboxylic functional groups were synthesized from isophoronediisocyanate (IPDI), polycaprolactone (PCL) (number-average molecular mass, $M_n = 2000$), 1,4-butanediol, BD, and 2,2′-bis-(hydroxymethyl)propionic acid (DMPA) according to the modified two-step procedure in the nitrogen atmosphere described in the literature [5,16]. The first step is the synthesis of prepolymer from PCL and IPDI in the solution of 1-methyl-2-pyrrolidinone for 4 h at 348 K. The second step was chain extension by DMPA and BD (28 h at temperatures gradually increasing from 333 to 363 K). DMPA was dissolved in 1-methyl-2-pyrrolidinone before addition into the reaction mixture. The reaction was monitored by the disappearance of the NCO signal in the IR spectra. The molar ratio of OH/NCO groups was 1.05/1. The concentration of functional groups varied from 0 to 0.45 mmol g^{-1} (Table 1).

2.1.2. Spin labelled PM prepolymers

The methacrylic (PM) components with tertiary amine functional groups were prepared from methyl methacrylate, *N*,*N*-dimethylaminoethyl methacrylate and hydroxylethyl methacrylate [5]. The concentration of functional groups varied from 0 to 0.45 mmol g^{-1} as in the PU prepolymer (Table 1). The small amount of OH groups (0.038 mmol g^{-1}) in PM copolymer was constant [5]. The 2,2,6,6-tetramethyl-4-aminopiperidin-1-yloxyl free radical (TAMINE) was covalently attached to the PM chain by the amide–ester interchange reaction [17]. The labelling was performed in benzyl alcohol solution of 2 mass% of PM, 10 mass% of sodium benzoxide and 0.1 mass% of nitroxide radical. The amide–ester interchange was allowed to proceed for 48 h at 303 K. Labelled PM copolymer without functional groups was precipitated with methanol and the other labelled copolymers by use of hexane in the mixture of benzyl alcohol and 2-butanone. The remaining unattached free radicals were removed by repeated precipitation of the copolymer. Spin labelled PM copolymers were annealed in vacuum for 48 h at 363 K or until no change of the ESR signal was detected. The concentration of spin labels did not exceed 10^{-5} mol g^{-1}.

2.1.3. Preparation of SIPNs

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 1,3,5 isocyanatohexamethylene diisocyanate (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 mixtures were cast as a film 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. SIPNs containing various concentrations of functional groups were prepared with PU and spin labelled PM (SIPN-0, SIPN-25, SIPN-35, SIPN-45) (Scheme 1). Prior to ESR measurements polymer films were annealed in vacuum for 48 h at 363 K.

2.1.4. Preparation of PU/PM mixtures

Labelled PM were mixed with PU containing the same concentration of functional groups in 1:1 mass ratio

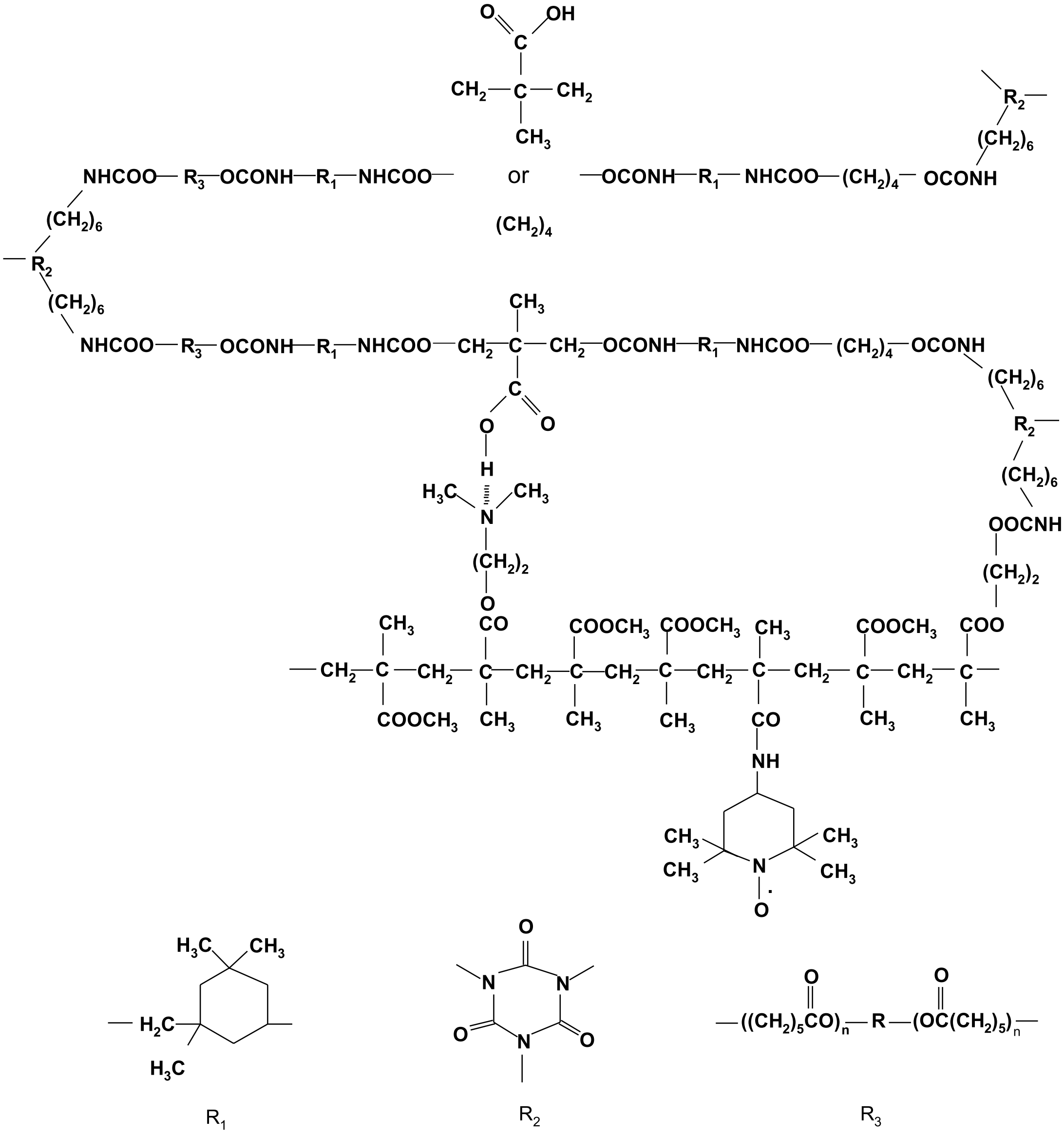
Table 1
Concentration of functional groups and molecular mass of PU and PM components

Sample	Conc. of func. groups (mmol g^{-1})	M_n of PU prepolymer (g mol^{-1})	M_n of PM prepolymer (g mol^{-1})
SIPN-0	0.00	12,300	11,200
SIPN-25	0.25	6600	11,400
SIPN-35	0.35	5600	10,500
SIPN-45	0.45	5300	10,700

in 2-butanone and stirred 24 h at 298 K. After the solvent had slowly evaporated off, mixtures (PU/PM-0, PU/PM-25, PU/PM-35, PU/PM-45) were annealed in a vacuum at 363 K for 48 h.

2.2. Methods

The molar mass averages of PU and PM samples were determined by size exclusion chromatography (SEC) on a Perkin–Elmer liquid chromatograph equipped with a differential refractometer as a detector. Two 5 μm PLgel columns, i.e. 10^3 Å and Mixed E with a precolumn (Polymer Laboratories), and THF as an eluent (1 mL min^{-1}) were used. Calibration for PU samples was conducted with polystyrene standards (Toyo Soda Manufacturing) and for PM samples with poly(methyl methacrylate) standards (Polymer Laboratories).



Scheme 1. R is a segment originating from the initiator (diol) in the polymerization of polycaprolactone. The value of *n* is estimated to be 8–9.

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.

The ESR spectra were recorded on a Varian E-109 X-band spectrometer operating at 9.76 GHz with 100 kHz modulation. The attenuation power (up to 5 mW) and modulation amplitude (0.1 mT) were adjusted well below saturation and distortion of the spectra. The spectra were collected with the following parameters: sweep width 16 mT, scanning time 25 s, 5–50 scans depending on the signal to noise ratio, 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 after approaching the corresponding temperature. The analysis of complex ESR spectra was based on the set of slow and narrow components. Narrow components were obtained by subtraction of the experimental slow spectra of the pure PM labelled prepolymer from the corresponding two-component ESR spectra. The percentage of accuracy related to the error in best fit of spectral components to the experimental data is about 3%.

The wide-angle X-ray diffractograms of the samples were taken by a Philips diffractometer with monochromatized Cu K_α radiation in the diffraction range $2\theta=4$–50°. Degree of crystallinity, $w_{c,x}$, was evaluated according to Kilian and Jenckel [18] in diffraction range $2\theta=6$–37°.

A Leica light microscope with digital camera was used for observations of thin specimen films.

3. Results and discussion

3.1. Motional heterogeneity of semi-interpenetrating networks with spin labelled PM component

Motional heterogeneity and the extent of miscibility in SIPNs containing various concentrations of functional groups was deduced by analysing motional behaviour of PM labelled component in a wide temperature range. The free radical covalently attached to the PM chain will help to assess interactions between the two polymer chains modified by the additional functional groups.

The ESR spectra of pure PM component were measured in the temperature range from 253 up to 393 K at intervals of 5 K. The upper limit of the measurements was determined by the decay of ESR signal. The spectra of the PM component, irrespective of the introduced functional groups, are characteristic of slow motion in the measured interval as shown for PM without functional groups (Fig. 1(a)). The outer maxima separation, $2A_{zz}$, of the broad lines changes very little. However, the intensity and the shape of the central line are changing above 350 K with an increase of functional groups concentration. (Fig. 1(b)). An increase of the central line intensity is a consequence of the faster local generation of free volume close to the temperature where the onset of a rapid motion of the spin label is expected. This slight motional difference between the PM-0 and functionalised PMs may be explained with differences in PM microstructure due to the introduction of functional groups via DMAEM. The change of PM microstructure with an increase of functional group concentration is also reflected in the lowering of T_g (Table 2).

If the labelled PM component is used for the preparation of SIPNs with the PU component the ESR line shapes of the covalently attached nitroxide are significantly different in the measured temperature range from 253 to 393 K. Characteristic two component spectra are observed for all the networks between ~330 and 393 K indicating that the PM segments partition in two motionally different environments in the network. Some representative spectra of SIPN-0 are shown in Fig. 2. The narrow component of the spectra arises from the fast motion of the PM segments plasticized by the PU motionally active segments, while the broad component corresponds to the motionally restricted PM segments in the hard domains, most probably composed of the pure PM chains and hard PU and PM chains. Similar partition was observed in the IPNs of labelled PVC and segmented PU [12].

The temperature at which the fast component is observed is determined by the functional groups concentration (Table 3). This temperature is marked as $T_{5mT(f)}$ and corresponds to the local segmental motion of PM segments plasticized by PU soft phase. A large fraction of the remaining PM segments retains slow motion up to 393 K. The lowest temperature at which a fast motion is detected is shifted to higher temperatures in functionalized networks. The highest shift is observed at 0.25 mmol g^{-1} (Table 3). The existence of two spectral components of labelled PM in all the networks above the characteristic temperature clearly shows that the networks are motionally heterogeneous or phase separated.

DSC measurements of SIPNs reveal the presence of two glass transitions characteristic of the phase separated system (Table 2). T_g of the PU component in the network is shifted toward higher temperatures as compared with the pure component. The T_g shift also increases by raising the concentration of functional groups from 0 to 0.45 mmol g^{-1}. However, PM component shows a slight decrease of T_gs in the networks. The T_g shifts of the PU component in the network are explained with crosslinking of the two polymers and additional intermolecular interactions.

Very broad glass transitions intervals, ΔT_g, of both pure PU prepolymer and SIPNs confirm heterogeneous morphology and consequently complex segmental motions as a result of incomplete mixing (Table 2). The ΔT_g of PU is broadened with increasing concentration of carboxylic groups (111 K for PU with 0.45 mmol g^{-1}). This phenomena can be explained with increasing compositional

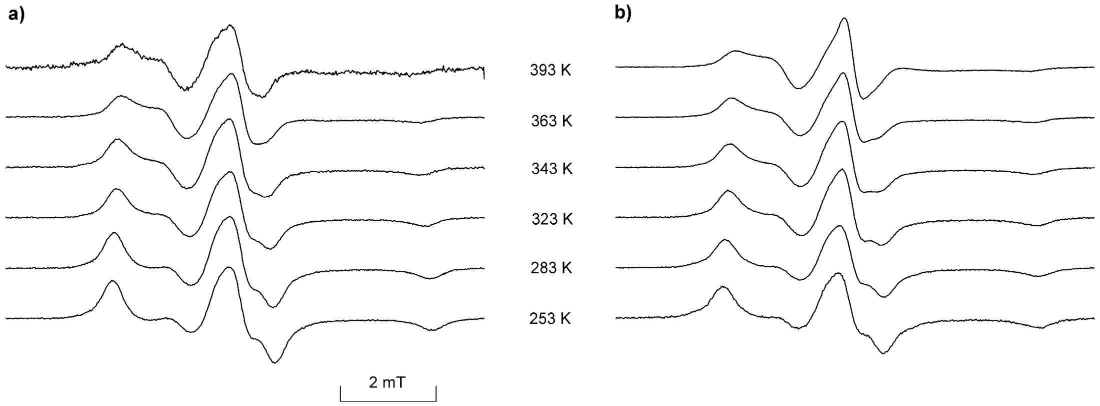


Fig. 1. Temperature dependent ESR spectra of spin labelled PM without functional groups (a) and PM with 0.45 mmol g^{-1} of functional groups (b).

heterogeneity induced by DMPA structural units and, consequently, broader distribution of intra- and intermolecular cooperative motions. In contrast to PU, ΔT_g range of pure PM prepolymers is quite narrow (33–40 K) irrespective of the concentration of incorporated tertiary amine groups. It appears that the structural units of *N*,*N*-dimethylaminoethyl methacrylate do not influence significantly the motional heterogeneity in PM component. The ΔT_g range in SIPNs is broad and comparable to the pure PU component. Similar observations of ΔT_g broadening due to the complex segmental dynamics were reported for polyurethane based IPNs [9]. However, ΔT_g range of PM component is narrower than in the mixtures and broader than in the pure PM prepolymer. This could be explained by the chemical crosslinking of PU component in SIPNs that restrict molecular motion of PM chains and thus contribute to narrower ΔT_g range than in the PU/PM mixtures.

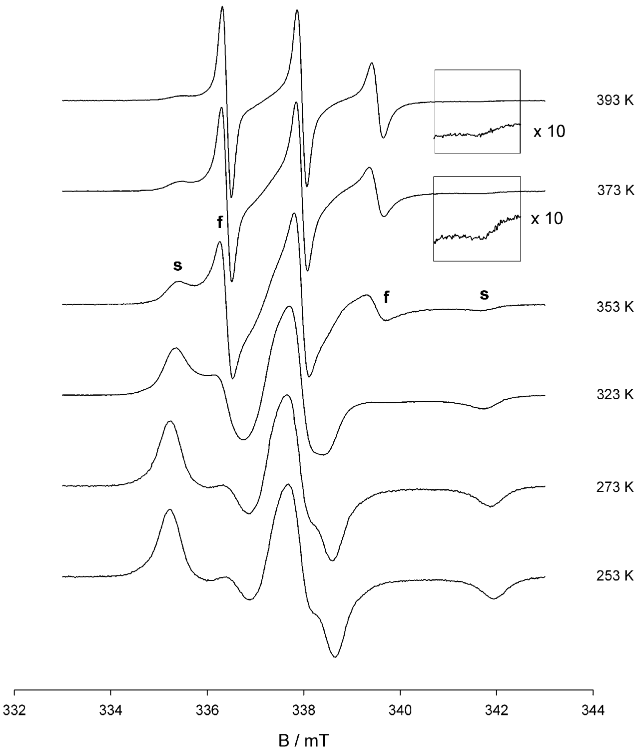


Fig. 2. Temperature dependent ESR spectra of spin labelled PM in SIPN-0. Two spectral components are marked with s (slow) and f (fast), respectively.

The temperature at which the ESR fast component appears and the corresponding $T_{5\mathrm{mT(f)}}$ shifts of the labelled PM component in SIPNs follow the same trend as T_g of PM component in the same network. Since the ESR method is very sensitive to segmental motion on a length scale shorter than those responsible for the glass transition temperature, discrete fast local segmental motion can be detected in a low percentage. The composed ESR spectra are used to deduce the extent of motionally separated phases or a fraction of slow/fast component of labelled PM copolymer in the networks. Thus the spin label method allows to characterize in detail the heterogeneity of segmental motions around T_g.

The fractions of fast/slow motion of labelled PM were derived by the subtraction of the slow motional component (as shown for SIPN-0 in Fig. 3). The subtracted narrow spectra of the PM component are typical for fast motion ($10^{-10}\ \mathrm{s} \leq \tau_R \leq 10^{-9}$ s). The analysis reveals the change of a fraction of fast/slow motion of PM segments at various temperatures depending on the content of functional groups. Characteristic spectra of the samples with various functional groups content at 363 K are given in Fig. 4.

Table 4 displays the fraction of the ESR slow/fast component of SIPNs at characteristic temperatures. The fraction of the slow component is decreasing with a rise of temperature due to the generation of free volume. However, free volume change is modulated by specific interactions in the network introduced by complementary functional groups. At each temperature in the range from 343 to 383 K the slow component is initially increasing with the introduction of functional groups and at concentration higher than 0.25 mmol g^{-1} the fraction of the slow component gradually decreases. Yet the fraction of the slow motion exceeds the amount of slow component of nonfunctionalised network. A decreased intensity of the slow component with temperature is explained with the change of complex interactions at elevated temperatures

Table 2
Glass transition temperatures, T_g, and glass transition temperatures ranges, ΔT_g, of pure PU and PM prepolymers (T_{g1}, ΔT_{g1}), PU and PM in SIPNs (T_{g2}, ΔT_{g2}) and mixtures (T_{g3}, ΔT_{g3}) determined by DSC

Conc. of func. groups (mmol g^{-1})	T_{g1} (K)[a]		ΔT_{g1} (K)[a]		T_{g2} (K)[a]		ΔT_{g2} (K)[a]		T_{g3} (K)		ΔT_{g3} (K)	
	PU	PM	PU	PM	PU	PM	PU	PM	PU	PM	PU	PM
0.00	249	373	84	40	257	377	76	62	252	364	66	82
0.25	264	368	105	33	285	378	95	50	276	352	85	58
0.35	269	367	106	33	297	372	115	48	290	351	86	40
0.45	278	366	111	33	304	368	117	37	315		110	

The accuracy of T_g determination is ±5 K.
[a] From Ref. [5].

Table 3
$T_{5mT(f)}$ values of ESR spectra of SIPNs and PU/PM mixtures and the corresponding τ_R values of the narrow component

Sample	$T_{5mT(f)}$ (K)	$\tau_R \times 10^9$ (s)[a]
SIPN-0	320	1.1
SIPN-25	340	1.2
SIPN-35	330	3.2
SIPN-45	325	3.8
PU/PM-0	305	0.9
PU/PM-25	320	1.2
PU/PM-35	315	1.0
PU/PM-45	310	0.9

The accuracy of T_{5mT} determination is ±3 K.
[a] Determined at 393 K.

[19]. Above ∼370 K the PM chains are approaching glass transitions temperature and the change of motional dynamics is expected.

Crosslinking of the PU component and specific interactions between the carboxylic groups bound to the PU hard segments and tertiary amine groups on the PM chains, restrict both PU and PM segmental motion. With an increased functional groups concentration more PM segments will interact with the PU hard segments increasing thus mass fraction of PU hard segments in PM rich phase [5]. As a result a portion of PM chains interacting with the soft phase is lowered. Further introduction of functional groups (above 0.25 mmol g^{-1}) drives the system to better miscibility and reduce phase separation. Reduced phase separation creates smaller domains and enhances a larger

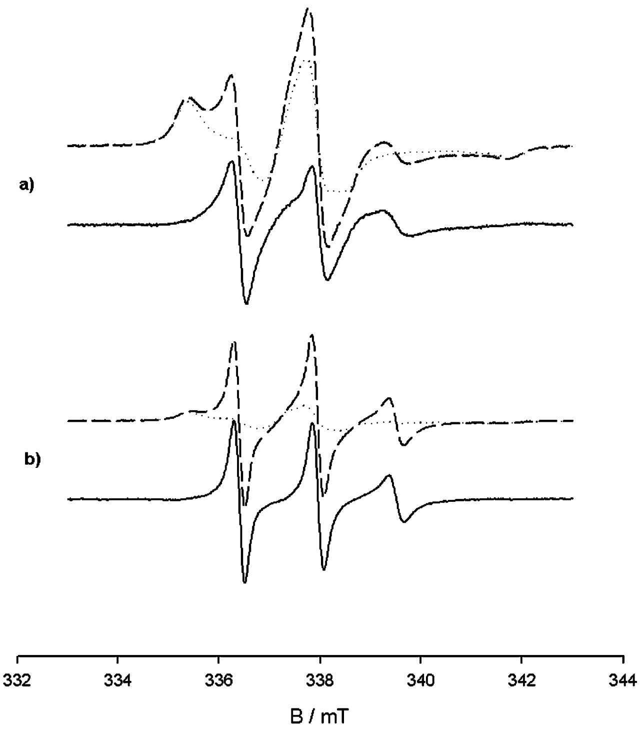


Fig. 3. Experimental (dashed) and fast component (solid) spectra of SIPN-0 after subtraction of the slow component (dotted) from the experimental spectra at 343 K (a) and 373 K (b).

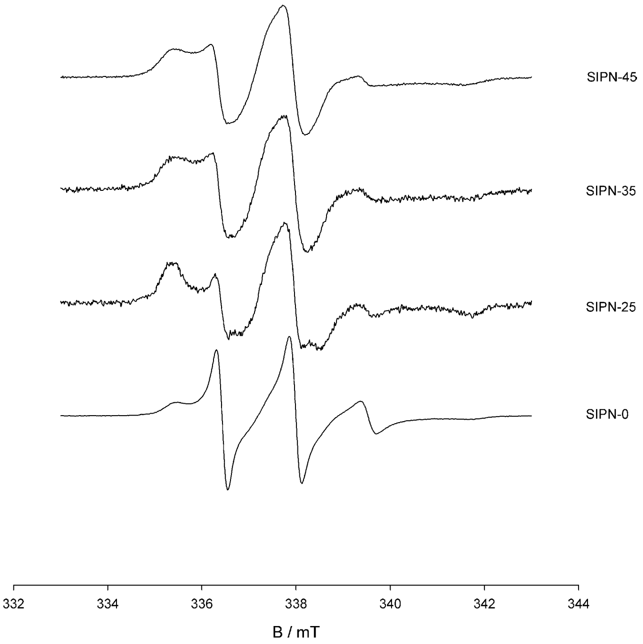


Fig. 4. ESR spectra of spin labelled PM in SIPNs with various functional groups concentration at 363 K.

fraction of PM segments [20] associated with the fast motion of PU segments. Crosslinking and additional hydrogen bonding in the networks also prevent three-dimensional ordering of PU soft segments as confirmed by the WAXD experiment and polarizing micrographs in SIPN-45. Previous experiments have shown that the pure PU component is partly crystalline [15] and that the crystallinity depends on the interactions imposed by functional groups. The lowering of the ordered phase is observed above the critical functional groups concentration.

Though the fraction of fast motion of PM segments in a closer contact with motionally active PU segments is increased at higher functional group concentration the rotational correlation times deduced from the corresponding spectral components [21] reveal somewhat slower motion of SIPN-35 and SIPN-45 as compared with the other networks (Table 3). The broadened line shapes of fast motion reflect the heterogeneity or motional distribution of the local environment that arise from a range of different intra- and intermolecular hydrogen bonding in the networks [12,22,23].

3.2. Motional heterogeneity of PU/PM mixtures with spin labelled PM component

Motional heterogeneity and the extent of interactions in the mixtures of PU and PM labelled components are compared with the semi-interpenetrating networks of the same composition. As already discussed spin labelled PM chains, irrespective of the functional groups concentrations, show one broad spectral component up to 393 K characteristic for the glassy polymer. The ESR spectra of 1:1 mixtures of the PM and PU polymer reveal broad line spectrum at low temperatures. However, at certain higher temperatures fast motion component superimposed on the broad spectrum appears. Some typical ESR spectra of PU/PM mixture without additional functional groups and with 0.25 mmol g^{-1} are shown in Fig. 5. Two spectral components are indicative for motionally different molecular environments in which the spin labelled PM chains are located. The narrow component is associated with the highly mobile chains or PM segments incorporated in the soft phase of PU component well below the glass transition temperature of the pure PM [12]. The broad component corresponds to rigid PM chains. Comparative DSC glass transition measurements for PU/PM mixtures are given in Table 2. The T_{g3} values corresponding to PU component in PU/PM mixtures are shifted to higher temperatures and are increasing with the functional groups concentration as in the case of pure component. An increase of T_g of PU component in the mixture is expected due to the interaction with PM segments with the higher T_g values. However, the T_g shifts are smaller as compared with the SIPNs of the same composition. The T_gs of PM component in the mixtures are decreased as listed in Table 2. Two transitions located between the T_gs of pure components indicate some interpenetration of polymer chains [24]. The broad ΔT_g range (Table 2) in each sample reveals compositional heterogeneity as in the case of SIPNs. The broadening depends on the functional groups concentration. However, ΔT_g range for PU component is narrower and broader for PM in comparison with the pure components. The

Table 4
Fractions of the ESR slow component of spin labelled PM in SIPNs and PU/PM mixtures as a function of functional groups concentration at different temperatures

Sample	343 K	353 K	363 K	373 K	383 K	393 K
SIPN-0	0.72	0.62	0.52	0.44	0.35	0.15
SIPN-25	0.96	0.93	0.85	0.75	0.46	0.19
SIPN-35	0.88	0.79	0.73	0.62	0.45	0.28
SIPN-45	0.82	0.75	0.66	0.57	0.42	0.24
PU/PM-0	0.65	0.60	0.51	0.45	0.41	0.35
PU/PM-25	0.80	0.72	0.66	0.61	0.56	0.51
PU/PM-35	0.75	0.70	0.60	0.55	0.50	0.45
PU/PM-45	0.70	0.65	0.55	0.49	0.45	0.40

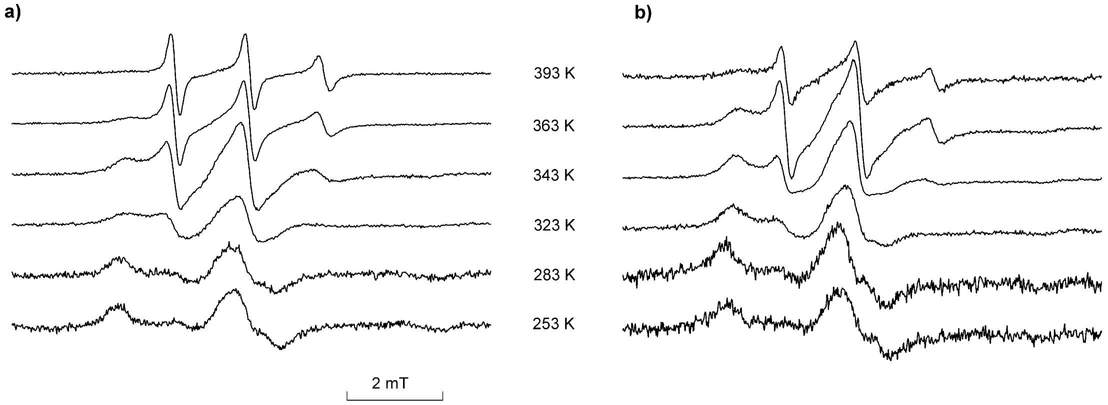


Fig. 5. Temperature dependent ESR spectra of spin labelled PM in PU/PM mixtures: PU/PM-0 (a) and PU/PM-25 (b).

differences in the ΔT_g range between PU/PM mixtures and SIPNs may be ascribed to different local composition or packing density in the absence of covalent bonding.

The occurrence of the composed ESR spectra above the characteristic temperature irrespective of the functional groups concentration is observed in all the mixtures. The trend of $T_{5mT(f)}$ shifts is the same as in the case of SIPNs, however the corresponding temperatures are lower (Table 3). The temperature at which the fast motion appears is closer to the PU glass transition and is a result of the PU soft phase that exert plasticising effect on the part of PM chains. Specific interactions between the carboxylic groups introduced into the PU hard segments and tertiary amine groups in PM chains reduce segmental motion of both PU and PM segments and $T_{5mT(f)}$ shifts to higher values as compared with the PU/PM-0 mixture.

Our results confirm that PU soft phase influence a part of PM chains, while the remaining PM slow segments represent a separated pure phase or/and a phase in which PU hard segments interact with PM segments. Obviously, motional heterogeneity is modulated by the inter- and intramolecular interactions or phase mixing. In order to quantify motional heterogeneity in terms of fast or slow motion the spectra were simulated and the percentage of slow motion is given in Table 4. As expected, the extent of slow motion is decreasing with temperature. However at each temperature the fraction of slow motion depends on the functional groups concentration following the same trend as in the case of SIPNs. Initially extent of slow motion increases with the introduction of functional groups and above certain concentration a fraction of slow motion is lowered. It may be suggested that the increased polymer hydrogen bonding interactions of PM segment and PU hard component at certain concentrations change the packing density due to the formation of looser local domain structure giving rise to a larger number of PM segment to assert fast motion. Thus the steric effects of DMAEM and DMPA at higher functional groups concentrations influence local interchain ordering and increase local free volume. The existence of a critical level of hydrogen bonding interaction above which molecular dynamics of PM segments or available free volume is changed may be compared with the effect of hydrogen bonding in blends of poly(*N*-vinylpyrrolidone) with poly(vinyl acetate-*co*-vinyl alcohol) [25].

The same trend in motional behaviour of both PU/PM mixtures and SIPNs seems to be dominated by functional groups interactions. Considerably large fraction of the slow motion at temperatures between 343 and 373 K in the SIPNs confirm enhanced interpenetration between the PU hard segments and PM chains generated by both chemical and physical crosslinks. At higher temperatures (at and above 383 K) slow component is substantially decreasing in SIPNs suggesting stronger influence of PU chains, which are above the glass transitions, on the PM segmental motion. The SIPNs appear to have much better chain interpenetration in comparison with polymer mixtures in which motional contribution of PM segments changed very little from 373 to 393 K. Since the thermally activated cooperative molecular motion for the pure PM component is not reached at 393 K, the broad component at these temperatures is largely dominated by the PM rich domains. The motional behaviour of SIPNs and PU/PM mixtures offer an insight into the generation of local segmental motion correlated to the polymer chain interpenetration and interaction in a wide temperature range. The analysis of segmental heterogeneity over a broad range of temperature may contribute to the better understanding of mechanical damping of the PU based networks.

3.3. Structural and morphological observations

SIPNs crystallizability and consequent morphology as a result of phase separation is examined by wide-angle X-ray diffraction and optical microscopy.

The WAXD curves without crystalline peaks and dark polarizing micrographs indicate amorphous character of freshly prepared SIPN samples. However, X-ray diffractograms of stored samples exhibit semicrystalline character in the case of SIPN-25 and SIPN-35, while SIPN-0 and SIPN-45 remain amorphous with three diffuse maxima (Fig. 6).

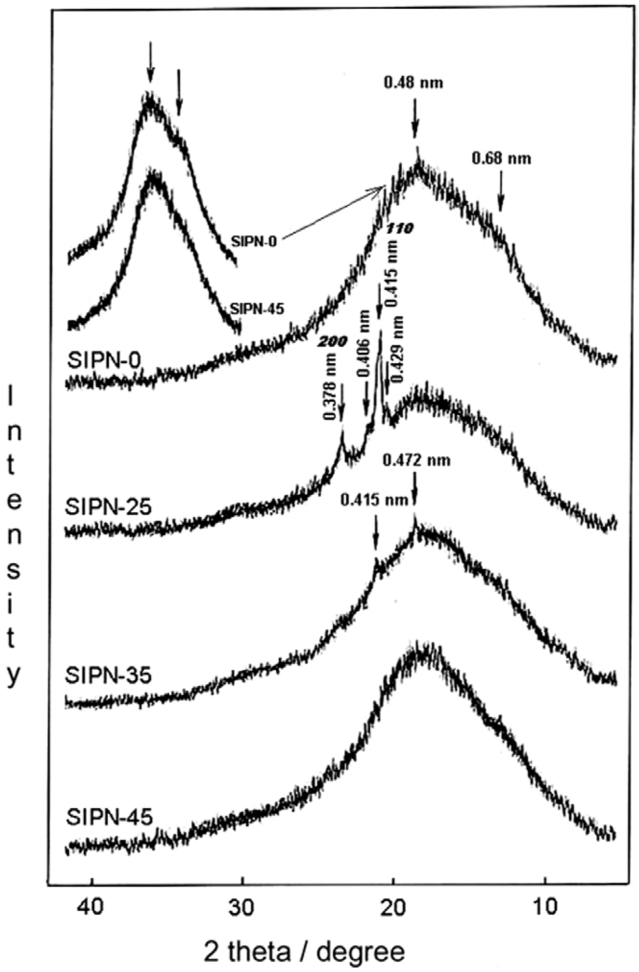


Fig. 6. Diffractograms of SIPN-0 (a), SIPN-25 (b), SIPN-35 (c), and SIPN-45 (d).

Two most intensive amorphous halos are partly overlapped and most likely originate from the superposition of amorphous haloes of the corresponding PU and PM components as in immiscible polymer blends. It is known from the literature that the diffractograms of polyester PUs exhibit one intensive amorphous halo in a region of diffraction angles were top position (18.3–20.0° 2Θ) depends on the soft/hard segment content ratio [26]. In this diffraction region different amorphous polyacrylates, as well as atactic PMMA, exhibit two intensive amorphous haloes. First diffraction halo at about 14.1° 2Θ ($s=1$ Å^{-1}, $d=6.28$ Å) contains intersegmental interchain component at ~13.4° 2Θ ($s=0.95$ Å^{-1}, $d=6.61$ Å), whereas second halo at ~17° 2Θ ($s=1.2$ Å^{-1}, $d=5.24$ Å) has purely intrasegmental, intrachain character [27,28]. The broad diffraction curve of the SIPN-0 could be resolved into two halos with the maxima at ~13° 2Θ ($d=0.68$ nm) and at 18.5° 2Θ ($d=0.48$ nm). Diffraction curves of SIPN-45 exhibit less intensive first halo at 13° 2Θ ($d=0.68$ nm) corresponding to PM component than the SIPN-0 indicating disruption of the PM domains due to the enhanced interaction with PU chains in SIPN-45 (Fig. 6). In other words better miscibility of polymer components in SIPN-45 is achieved. The disruption of the PM domains in SIPN-45 complements increased PU–PM interpenetration derived from the ESR spectra. The diffractogram of SIPN-25 exhibits additional four sharp diffraction peaks: $d=0.429$, 0.415, 0.406 and 0.378 nm corresponding to crystalline PCL phase (Fig. 6) [29–31], while diffractogram of SIPN-35 exhibits only two very weak reflection ($d=0.472$ and 0.415 nm) superimposed on the amorphous diffraction curve. The appearance of only few crystalline PCL reflections (110 (0.415 nm), 111 (0.406 nm) and 200 (0.378 nm)) is in agreement with those reported by Kloss et al. [32] in copolymers derived from PCL 2000. The degree of crystallinity of SIPN-25 ($w_{c,x}=5\%$) is higher than that of SIPN-35 ($w_{c,x}=1.5\%$). This difference is significantly larger if the crystallinity of SIPN samples is recalculated on the basis of pure PU component. Taking into consideration the composition of SIPN (1:1), the degree of crystallinity of pure PU components would be about $w_{c,x}=10\%$ in SIPN-25 and $w_{c,x}=3\%$ in SIPN-35. WAXD analysis indicates different degree of ordering which decreases in order: SIPN-25 > SPN-35 > SIPN-0 ≥ SIPN-45.

Bogdanov et al. [31] have reported that only soft domains of PU with longer PCL blocks ($M_w > 2000$) could crystallize immediately after solvent evaporation, while PU with shorter PCL blocks ($M_w = 2000$) are completely amorphous. However, soft domains of PU with PCL 2000 crystallize during storage at room temperature for more than 2 months. It could be concluded that the crystallization of hard domains in PU is disabled since the cast temperature is lower than T_g of hard segments in SIPNS (Table 2). The introduction of DMPA into hard segments at first stage contributes to the phase separation and consequently to the ordering of soft segments. With further increase of DMPA content the inter- and intramolecular interactions in SIPNs prevail leading to the disruption of domain structure and prevent crystallization of soft segments.

Microphase separation enables a formation of soft and hard segment domains. Since in the present case hard to soft segment mass ratio is 1:1 bicontinuous phase could be expected [31]. In such a system of bicontinuous soft/hard domains radial growth of soft fringed lamellae leads to the formation of spherulites during the crystallization process. Polarization microscopy confirms the presence of spherulites depending on the functional groups content. SIPN-0 and SIPN-45 exhibit under crossed polars mainly dark field or the absence of any morphological form. Contrary to the completely dark fields of SIPN-45 sample, SIPN-0 reveals sporadic light spots in some dark field areas indicating a tendency of formation of ordered morphological forms. Polarizing micrographs of SIPN-25 (Fig. 7(a)) and SIPN-35 (Fig. 7(b)) samples reveal spherulitic morphology with non-impinging ring spherulites. SIPN-25 taken with lower magnification shows interconnected spherulites (Fig. 8(a)) as can be clearly seen in the contrasted optical micrograph

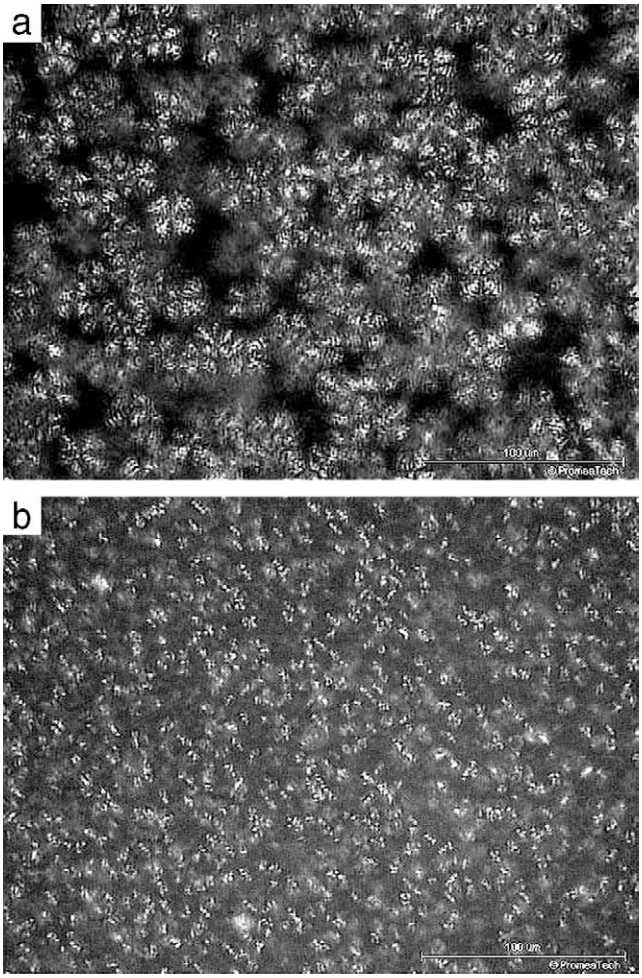


Fig. 7. Polarizing micrographs of SIPN-25 (a) and SIPN-35 (b).

(Fig. 8(b)). Separated ring spherulites of SIPN-25 sample (average spherulites diameter about 25 µm) are considerably larger than those of SIPN 35 (average spherulites diameter about 8 µm). This difference in the spherulite size corresponds to the difference in the crystallinity of these samples estimated by WAXD. The polarizing micrographs confirm different degree of morphological ordering which decreases in order: SIPN-25 > SPN-35 > SIPN-0 ≥ SIPN-45.

4. Conclusions

The ESR spin label method was used to investigate motional heterogeneity and phase transitions in SIPNs and mixtures of segmented polyester polyurethane prepolymer (PU) and polymethacrylic (PM) prepolymers depending on the functional group concentration. Carboxylic groups were incorporated into the PU hard segments and tertiary amine groups into the PM prepolymer. Spin labelled PM chains are sensitive to the intermolecular interactions and reflect molecular dynamics of the network on the segmental level.

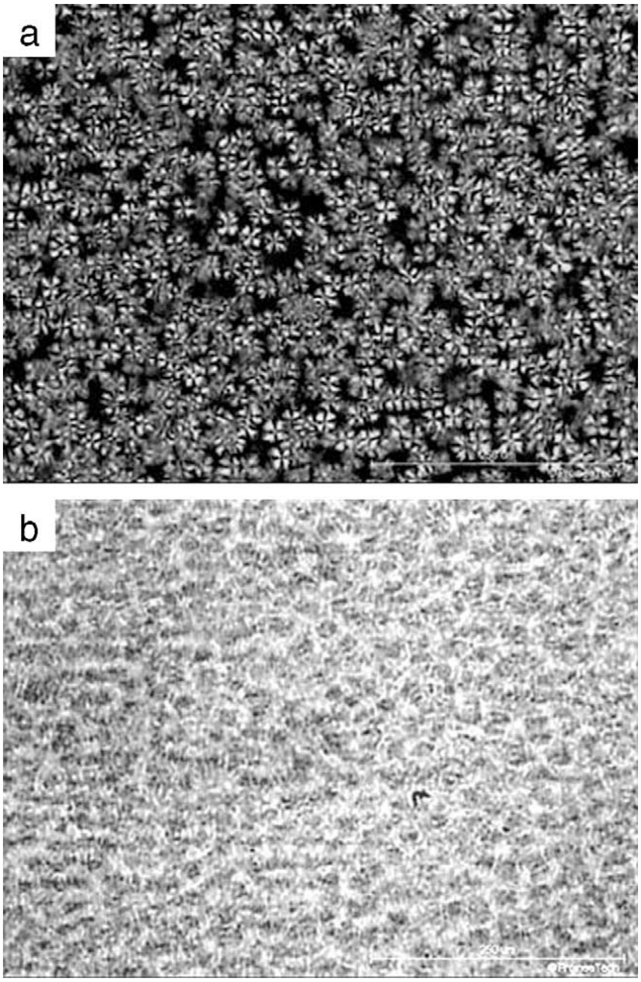


Fig. 8. Polarizing (a) and contrasted optical micrograph (b) of SIPN-25 with lower magnification.

Both SIPNs and PU/PM mixtures are motionally heterogeneous as revealed from the two component ESR spectra of spin labelled PM. The fast motion corresponds to the segmental motion of the PM component influenced by the PU soft phase. The PM chains that retain slow motion contribute to the slow component of the spectra. The extent of fast/slow motional phase depends on the concentration of functional groups. In SIPNs motional heterogeneity is additionally modulated by the crosslinking agent. The fraction of slow motion is initially increasing with the introduction of functional groups and above 0.25 mmol g^{-1} is decreasing. With an increase of hydrogen bonding interactions of PM segments and PU hard component above a critical concentration, due to the change of packing density, a larger number of PM segments asses fast motion. According to the temperature change of the slow motion and the extent of this motion PU impart stronger interactions on the PM segmental motion in SIPNs than in the mixtures.

The temperature intervals, ΔT_g, of the glass transition reveal compositional heterogeneity in both SIPNs and mixtures, which depends on the functional groups concentration.

Polarizing micrographs and WAXD measurements confirm that the functional groups strongly affect sequence ordering and phase separation. The degree of ordering is decreasing in order: SIPN-25 > SIPN-35 > SIPN-0 ≥ SIPN-45. The broad diffraction maximum of SIPN-45 and the diffractogram of SIPN-25 with additional sharp maximum confirm disruption of the ordered domains due to the increased interpenetration of PM and PU chains in the network.

Acknowledgements

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References

[1] Sperling LH. In: Klempner D, Sperling LH, Utracki LA, editors. Interpenetrating polymer networks. ACS symposium series, vol. 239. Washington, DC: American Chemical Society; 1994.

[2] Hourston DJ, Song M, Schafer FU, Pollock HM, Hammiche A. Polymer 1999;40:4769–75.

[3] Natchimuthu N, Rajlingam P, Radhakrishnan G, Francis DJ. J Appl Polym Sci 1990;41:3059–68.

[4] Anžlovar A, Anžur I, Malavašić T. J Polym Sci Polm Chem 1996;34: 2349–61.

[5] Anžlovar A, Žigon M. J Polym Sci Pt B-Polym Phys 2002;40:115–23.

[6] Patsis A, Xiao HX, Frisch KC, Al-Khatib S. J Coat Technol 1986;58: 41–7.

[7] Vatalis AS, Delides CG, Grigoryeva OP, Sergeeva LM, Brovko AA, Zimich ON, Shtompel VI, Georgoussis G, Pissis P. Polym Eng Sci 2000;40:2072–85.

[8] Hourston DJ, Schafer FU, Walter NJ, Gradwell MHS. J Appl Polym Sci 1998;67:1973–85.

[9] Bershtein VA, Yakushev PN, Karabanova L, Sergeeva L, Pissis P. J Polym Sci Pt B-Polym Phys 1999;37:429–41.

[10] Sperling LH, Fay JJ. Polym Adv Technol 1991;2:49–56.

[11] Veksli Z, Andreis M, Rakvin B. Prog Polym Sci 2000;25:949–86.

[12] Schlick S, Harvey RD, Alonso-Amigo MG, Klempner D. Macromolecules 1989;22:822–30.

[13] Čulin J, Veksli Z, Anžlovar A, Žigon M. Polym Int 2003;52:1346–50.

[14] Čulin J, Frka S, Andreis M, Šmit I, Veksli Z, Anžlovar A, Žigon M. Polymer 2002;43:3891–9.

[15] Čulin J, Andreis M, Šmit I, Veksli Z, Anžlovar A, Žigon M. Eur Polym J 2004;40:1857–66.

[16] Tirpak RE, Markusch PH. J Coat Technol 1986;58:49–54.

[17] Veksli Z, Miller WG, Thomas EL. J Polymer Sci: Polym Symp 1976; 54:299–313.

[18] Kilian HG, Jenckel E. Kolloid-ZZ Polym 1959;165:15–31.

[19] Coleman MM, Lee KH, Skrovanek DJ, Painter PC. Macromolecules 1986;19:2149–57.

[20] Hourston DJ, Schafer FU. J Appl Polym Sci 1996;62:2025–37.

[21] Gross SC. J Polym Sci Pt A-1 1971;9:3327–35.

[22] Chen WP, Schlick S. Polymer 1990;31:308–14.

[23] Chen WP, Kenney DJ, Frisch KC, Wong SW, Moore R. J Polym Sci Pt B-Polym Phys 1991;29:1513–24.

[24] Fox D, Allen R. In: Mark HF, Bikales NM, Overberger GC, Menges G, editors. Encyclopedia of polymer science and engineering, vol. 3. New York: Wiley; 1985. p. 758–75.

[25] Cowie JMG, McEwan I, McEwen IJ, Pethrick RA. Macromolecules 2001;34:7071–5.

[26] Van Bogart JWC, Gibson PHE, Cooper SL. J Polym Sci Pt B-Polym Phys 1983;21:65–95.

[27] Lovell R, Mitchell GR, Windle AH. Trans Faraday Soc 1979;68: 46–57.

[28] Windle AH. Pure Appl Chem 1985;11:1627–38.

[29] Bittiger H, Marchessault RH, Niegisch WD. Acta Cryst B 1970;26: 1923–7.

[30] Liaw D-J. J Appl Polym Sci 1997;66:1251–5.

[31] Bogdanov B, Toncheva V, Schacht E, Finelli L, Sarti B, Scandola M. Polymer 1999;40:3171–82 (and references therein).

[32] Kloss J, Munaro M, de Souza GP, Valente Gulmine J, Wang SH, Zawadzki S, Akcelrud L. J Polym Sci Polm Chem 2002;40:4117–30.