

SEMI-INTERPENETRATING POLYMER NETWORKS OF POLYURETHANE AND POLY(VINYL CHLORIDE)

Thermal stability assessment

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A series of semi-interpenetrating polymer networks (semi-IPN) of polyurethane (PU) and poly(vinyl chloride) (PVC) has been obtained by prepolymer method and characterised by FTIR; morphological features were examined by SEM–EDS. It has been found that PVC spherical aggregates are dispersed in the PU matrix, but Cl atoms location indicates partial miscibility of both polymers at the interphase which is probably due to hydrogen bonding and/or dipole–dipole interactions. The PVC component influences the phase behaviour of PU's hard segments, as evidenced by DSC results. Thermogravimetric analysis (TG) reveals a complex, multi-step decomposition process with the main mass loss at 503–693 K, while the DTG maxima are located between 540 and 602 K.

Keywords: polyurethane, PVC, semi-IPN, thermal stability

Introduction

In the search for novel polymeric materials one considers interpenetrating polymer networks (IPN) as promising systems that show improved properties, e.g. enhanced impact resistance and crystallisation rates [1, 2]. Different approaches have been successfully implemented to develop complex IPN that are systems prepared by polymerizing a monomer and its cross-linking agent in the presence of a cross-linked polymer network of a different composition. Such systems can be prepared sequentially, in which one network is prepared and swollen with the second set of reactant (SeqIPN), or they can be prepared by simultaneous reaction of all of the constituents (SimIPN). An interesting group of IPN constitute semi-IPN (pseudo-IPN) which are described as systems made of cross-linked polymer and a linear or branched polymer; the both components are not covalently linked. In this respect, application of polyurethanes (PU) for different IPNs becomes an interesting task since they exhibit excellent mechanical (elastical) properties provided that morphological control is maintained [3–6] since the fundamental phenomenon associated with all IPNs is that phase separation occurs during the reaction. The timing and the extent of phase separation are determined by the thermodynamic immiscibility between the components, and this immiscibility changes during the course of the reaction. The extent of phase separation is limited by the spatial scale over which interpenetration occurs at the onset

of phase separation, and this in turn is related to the rates of polymerisation in the system [7]. Such a complex morphology strongly influences the properties of an IPN, including the thermal properties and flammability. Continuing our interest on PU materials and poly(vinyl chloride) (PVC) we decided to investigate the thermal properties of PU–PVC semi-IPNs – such a study constitutes an essential step in further understanding of the flame retardation effect by PVC in blends with other polymers, as described earlier [8]. Hence, in this work we have obtained by prepolymer method a series of well-defined PU–PVC semi-IPNs, based on (i) partially polymerised diphenylmethane-4,4'-diisocyanate (PMDI), polyoxypropylenediol and 1,4-butanediol as a low-molecular chain extender, and, (ii) PVC, and characterised the thermal stability of the obtained PU-based materials.

Experimental

Materials

For synthesis of semi-IPNs partially polymerised 4,4'-diphenylmethane diisocyanate (MDI, 31% of free isocyanate groups in relation to the pure MDI) (Zachem Bydgoszcz, Poland), polyoxypropylenediol (POPD, $M=2000$, 750 or 450) (Rokita S.A., Brzeg Dolny, Poland), 1,4-butanediol (BD) (Merck KGaA, Darmstadt, Germany), and 1-allyl-2-methylimidazole (catalyst), (Z.Ch. Zachem, Bydgoszcz, Poland) were used. Ethyl acetate (POCH) was purified by distillation and used as

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a solvent during polymerisation. Poly(vinyl chloride) (PVC 68 Pbs) was product of Chemical Company 'Dwory S.A.' in Oswiecim, Poland.

Preparation

Segmented PU were prepared by a two-step (pre-polymer) method, according to the general procedure: in a thermostated reactor, MDI, POPD and PVC were reacted at 65°C for 2 h. The obtained prepolymer was dried under vacuum, and then subjected to further polymerisation with BD in the presence of catalyst (0.5 mass%). The reaction time was 30 min. MDI/diol ratio was determined equivalently.

Detailed description of the obtained samples is given in Table 1.

Table 1 Samples description

Sample number	Molar mass of POPD/ g mol ⁻¹	PVC content/ mass/mass%
1		0
2		5
3	450	10
4		15
5		20
6		0
7		5
8	750	10
9		15
10		20
11		0
12		5
13	2000	10
14		15
15		20

Techniques

Thermogravimetry (TG)

Thermogravimetric analysis was performed on a Netzsch TG 209 thermal analyser, operating in a dynamic mode at a heating rate of 10 K min⁻¹, sample mass – ~6 mg, atmosphere – argon, open α -Al₂O₃ pan.

Differential scanning calorimetry (DSC)

For the DSC measurements a Netzsch DSC 200, operating in dynamic mode, was employed. Samples of ~5 mg mass were placed in sealed aluminium pan. Heating rate of 10 K min⁻¹ was applied; prior to use the calorimeter was calibrated with In, Hg, Sn and Bi standards and an empty aluminium pan was used as a reference. Liquid nitrogen was used as cooling medium.

Fourier transform infra-red spectroscopy (FTIR)

FTIR spectra were recorded on finely ground dispersions of PU–PVC IPN samples in spectroscopic grade KBr by using a Biorad FTS 60VM spectrometer, operating in the spectral range of 4000–400 cm⁻¹ with the number of scans equal 30 (resolution of 2 cm⁻¹).

Scanning electron microscopy–energy dispersive spectrometry (SEM–EDS)

A scanning electron microscope JSEM Jeol 5400, equipped with energy dispersive spectrometer (EDS) (LINK ISIS 300), was used to investigate the surface morphology and composition of carbon-coated samples at the energy of the electron beam of 20 kV.

Results and discussion

FTIR spectroscopy was applied to determine the structure of semi-IPNs obtained – characteristic spectrum, representative for all IPNs, is displayed in Fig. 1.

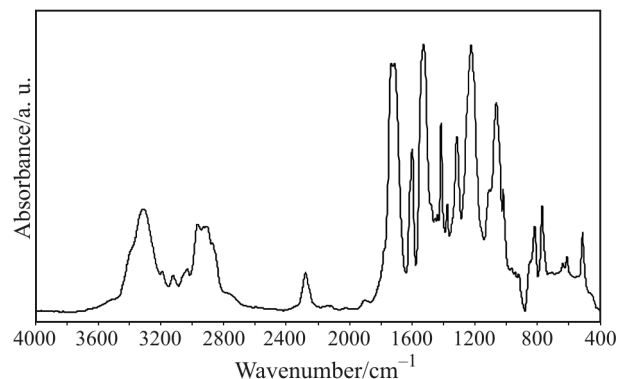


Fig. 1 FTIR spectrum of sample 8

The description of absorption bands is given in Table 2.

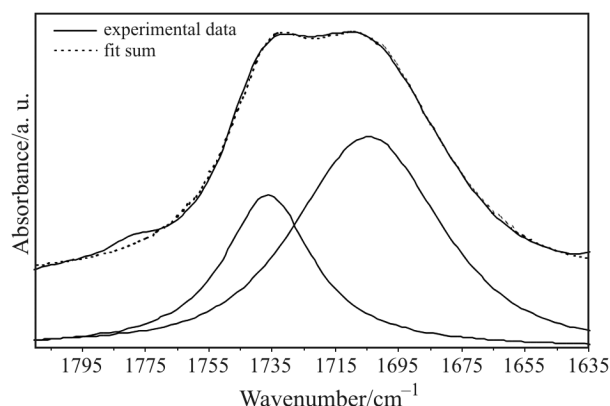
It can be seen that absorption band originating both from PU and PVC are present in the FTIR spectrum.

Figure 2 shows carbonyl absorption for sample 8 – the two peaks related to free and bonded carbonyl groups were separated by curve fitting method using the Gauss–Lorentz asymmetric function that adjusts a number of spectrum's parameters (number of peaks, their shape (width, height, etc.) to obtain the best fit of the sum of the calculated peaks to that of the measured ones. The goodness-of-fit is described by:

$$\chi^2 = \frac{\sum_{i=0}^n \left(\frac{\text{actual}_i - \text{calculated}_i}{\text{RMSnoise}} \right)^2}{(n - f)}$$

Table 2 Assignment of IR bands of PU–PVC semi-IPNs

Wavenumber/cm ⁻¹	Type of vibration
3320	N–H stretching
3033	C–H stretching (aromatic)
2910	CH ₂ asymmetric stretching
2279	C=N stretching (isocyanate group)
1731	C=O stretching (not bonded hydrogen bond)
1710	C=O stretching (bonded hydrogen bond)
1598	C–N–H bonding
1598	C–N stretching
1525	C–C stretching (aromatic)
1312	C–H deforming in plane (aromatic)
1061	C–O–C stretching
768	C–Cl stretching

**Fig. 2** Deconvolution of C=O absorption band into its components of sample 8

where the ‘actual’ and ‘calculated’ values are the measured and calculated data, respectively. The ‘RMSnoise’ is the estimated root mean squared noise in the ‘actual’ data over the fitted region. The variable n is the number of data points in the fitted region and f is the total number of variables from all the peaks and baseline functions. Thus, $n-f$ is the number of degrees of freedom.

The Levenberg–Marquardt algorithm iteratively adjusts every variable for each peak in an attempt to minimize the χ^2 (sometimes called reduced chi-squared). As can be deduced from the above equations, χ^2 is a weighed difference measure between the actual and measured data.

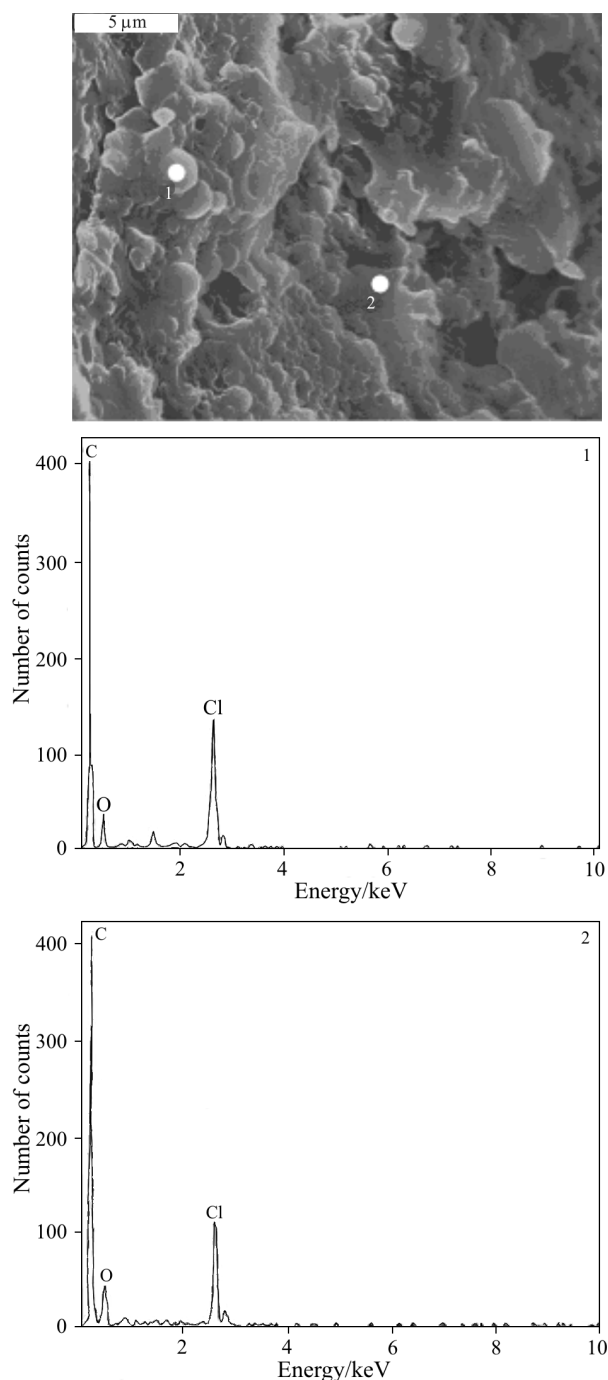
Thus, in 1700–1740 cm⁻¹ region two overlapping bands are visible. They come from stretching vibrations of free carbonyl groups (weaker band) and hydrogen bonded (with –NH– groups) carbonyl groups (stronger band), respectively [9–11].

It has been reported in literature that chlorinated polymers are in many cases miscible with polymers that

contain carbonyl group due to H-bonding between the C=O groups and α -hydrogen of chlorinated polymer [12, 13] or a dipole–dipole interactions [14–16].

SEM–EDS data make it possible to describe both the morphology and perform chemical analysis, as it can be seen in Fig. 3.

One can observe spherical aggregates of PVC dispersed in polyurethane matrix. EDS analysis results show the presence of chlorine atoms both in

**Fig. 3** SEM microphotograph ($\times 6000$) and EDS analyses of sample 5

PVC aggregates and in PU matrix surface – this finding may be associated with (partial) miscibility of PVC in PU matrix.

Thermal stability, as investigated by TG, shows a multi-step decomposition profile of the PU–PVC semi-IPNs (Fig. 4).

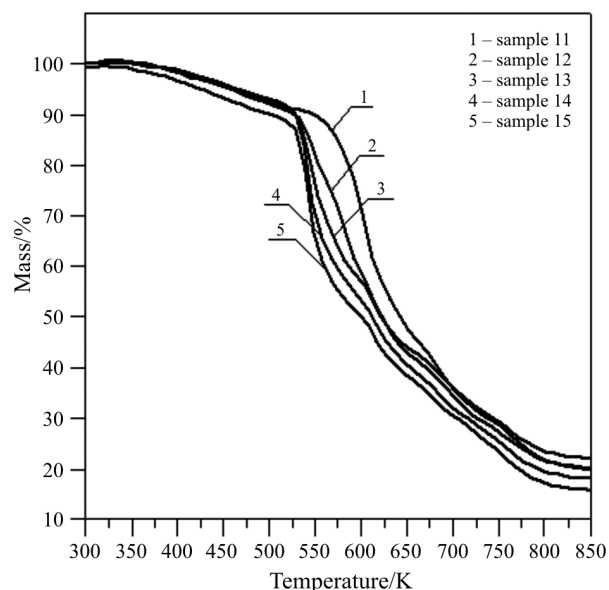


Fig. 4 Thermogravimetric profiles of samples 11, 12, 13, 14 and 15 at 10 K min^{-1}

Three regions of mass loss have been found on TG curves. First in the range of 313–503 K (12% mass loss), second between 503 and 693 K (50% mass loss) and third one in the range of 693–863 K (14% mass loss).

First region is related to initiation of decomposition, but small evaporation of the solvent used during the synthesis can not be ruled out. In the second region main decomposition occurs, during which the rate of decomposition is the fastest. The third region is related to the final decomposition process, probably associated with formation of stable residue due to cross-linking reactions [17].

It has been found that PVC decreases temperature of maximum rate of decomposition (DTG maximum) in comparison to pure PU, but this phenomenon was already observed in other polymeric systems with fire retardants. On the other hand during thermal decomposition PVC evolves hydrogen chloride that acts as radical scavenger inhibiting thus burning process [8, 18].

Moreover, for pure PUs, along with an increase of molecular mass of POPD the amount of solid residue also increases (Table 3).

This behaviour is probably connected with the structural features of the multiphase PU morphology. Soft segments (POPD) form a flexible matrix between the hard domains that in turn provide physical

Table 3 Amount of solid residue and values of DTG maximum temperature of the decomposition process of semi-IPN PU–PVC

Sample number	Amount of solid residue/%	Temperature of DTG maximum/K
1	17.2	601
2	18.4	584
3	18.1	546
4	18.3	543
5	15.3	541
6	18.8	602
7	19.7	581
8	19.0	544
9	15.3	543
10	14.0	542
11	19.8	602
12	18.8	581
13	21.2	541
14	17.5	542
15	15.8	540

cross-linking a complex, phase-segregated morphology is formed that varies with the temperature.

DSC analysis results in the temperature range of 213–523 K show that, due to complex PU morphology, a number of thermal events occur (Fig. 5).

Generally, glass transition has been observed – for samples 1 and 5 laying in range 393–423 and 413–433 K, for samples 6 and 10 in range 403–423 and 423–433 K, whereas for samples 11 and 15 in range 393–413 and 413–433 K, respectively. These results show shifts of glass temperature ranges toward higher temperatures in related to pure PU. Moreover, for samples 1, 5 and 6, relaxation of enthalpy processes accompanies glass transitions. Not-distinct glass transitions were due to cross-linked structure of examined polymers – in the presence of cross-links, single chains cannot freely move.

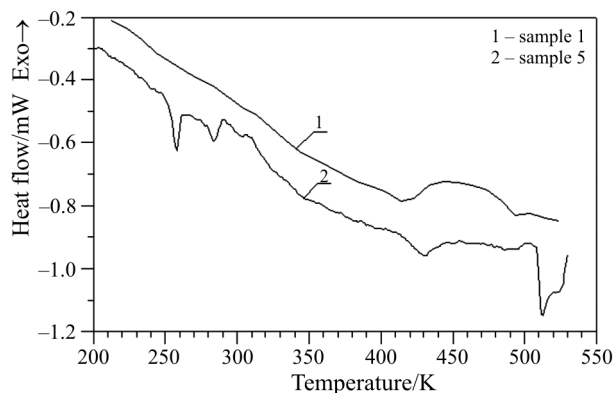


Fig. 5 DSC curves of samples 1 and 5 at 10 K min^{-1}

Apart from glass transitions endothermic peaks were observed on DSC curves above 200°C. These peaks are connected with melting process of hard segments in PU phase; in the presence of PVC they shift toward lower temperatures.

Conclusions

Semi-IPN of PU and PVC that have been obtained by pre-polymer method show a complex, multi-stage thermal degradation behaviour, as evidenced by TG method, that is probably connected both with the bond dissociation energy of PU and PVC, and with the structural features of the multiphase morphology. It has been observed by SEM method that spherical aggregates of PVC are dispersed in PU matrix – EDS analysis results show the presence of chlorine atoms both in PVC aggregates and in PU matrix surface – this finding may be associated with (partial) miscibility of PVC in PU matrix. In the PU–PVC IPNs PU soft segments form a flexible matrix between their hard domains that in turn provide physical cross-linking; PVC macrochains interact through hydrogen bonding or dipole–dipole forces with PU.

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