The influence of solvent on the properties of solutions and on the structure of films based on a copolymer of styrene and acrylonitrile, polyurethane, and their blends

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Selected from International Polymer Science and Technology, 41, No. 2, 2014, reference KR 13/04/24; transl. serial no. 17098

Extensive theoretical and experimental data concerning assessment of the influence of the solvent on the processing properties of solutions of polymers and the service characteristics of materials produced by their processing – adhesives, mastics, sealants, fibres, and non-woven materials – have now been obtained [1-10]. However, the presented data largely concern the influence of solvents on the rheological behaviour of solutions of polymers and on the properties of materials based on them for specific applied problems.

In order to broaden notions concerning the role of the solvent in the creation of polymeric materials with a specified combination of properties that are obtained by processing via solution, in the present work an investigation was made of the influence of the solvent on the structure and properties of polymer films formed from solutions of individual polymers – thermoplastic polyurethane (TPU), a copolymer of styrene and acrylonitrile (SAN), and their blends.

The choice of polymers was dictated by the wide use of TPU as the base of solution adhesion composites for the furniture and footwear industry, and of SAN in the manufacture of non-woven materials by the electroforming method [2, 4, 7]. It has been reported [7, 11] that the use of TPU/SAN polymer blends makes it possible to broaden the areas of application of materials obtained by processing solutions based on them – adhesive compositions and filter materials – by improving their service characteristics.

The investigation was conducted on weak and concentrated solutions and films based on polyurethane thermoplastic elastomer Desmocoll 400 (Bayer) (\(M_w = 1.0 \times 10^5\)) and styrene-acrylonitrile copolymer SAN 350N (Kumho) (\(M_w = 1.0 \times 10^5\)), and their blends with ratios of the components PU:SAN = 10:90, 20:80, 30:70, 50:50, 80:20 wt%.

Measurement of the viscosity of the weak solutions was done on an Ostwald VPZh-2 viscometer [5, 12] in organic solvents of different chemical classes: ethyl acetate (EA), methyl ethyl ketone (MEK), N,N-dimethylformamide (DMF), tetrahydrofuran (THF), and acetone (A). The investigated concentrations of the solutions lay in the range 0.1-2.0 g/dL.

The films were produced in petri dishes by casting from polymer solution (the concentration amounted to 10 wt%), with subsequent removal of the solvent at constant temperature and humidity.

The dynamic mechanical analysis of specimens was conducted on a DMA 242 C unit (Netzsch) at frequencies of 0.1, 0.5, and 1 Hz. Calorimetric investigations of the materials were carried out using a DTAS-1300 thermal analyser in the temperature range from -90 to 140°C. The heating rate was 20°C/min. The accuracy of temperature measurement was ±0.5°C.
Study of the dynamics of molecular motions in the polymers was done by electron paramagnetic resonance (EPR), which was based on analysis of the rotational mobility of paramagnetic particles – stable nitroxyl radical 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) – in the studied medium. The radical was introduced into films from vapour at a temperature of 25°C to a concentration of \(10^{-3}\) mol/L. EPR spectra were recorded in the absence of saturation, which was checked against the dependence of signal intensity on the power of the microwave field. The rotational mobility of the probe was characterised by the time of correlation \(\tau\), which determines the average residence time of the particle in a certain spatial orientation. The EPR spectra were recorded in the absence of intermolecular interaction (exchange and dipole). The correlation time was determined by means of the formula:

\[
\tau = \Delta H_+ \left( \frac{I_-}{I_+} - 1 \right) \times 6.65 \times 10^{-10}
\]

where \(\Delta H_+\) is the width of the spectrum component in a weak field, and \(I_+\) and \(I_-\) are the intensities of the components in a weak and in a strong field respectively [13].

Along with qualitative determination of the structure of complex molecules, IR spectroscopy makes it possible to obtain quantitative data on the content of particular groups of atoms, bonds, and their combination in a molecule. In order to establish that hydrogen bonds are actually formed in binary TPU/SAN systems between functional urethane and nitrile groups, IR spectra of films (40 \(\mu\)m thick) obtained from solutions of the individual polymers and from their blends were recorded on a Spectrum 100 IR Fourier spectrometer (PerkinElmer). The spectra were taken in transmitted light in the range 4000-450 cm\(^{-1}\) and in reflected light on a horizontal attenuated total reflectance (HATR) accessory (PerkinElmer) using a ZnFe 45° flat plate in the range 4000-650 cm\(^{-1}\).

The structure formation in the solutions is determined by the nature of the solvent used, the main reason for differences in the structure of the obtained materials being the interaction of the polymer with the solvent, and the accepted criterion of solvent activity in the scientific community is the thermodynamic affinity between the solvent and the dissolved substance [2, 3, 5, 7, 9, 10].

In the present work, on the basis of viscometric investigations, for quantitative assessment of the thermodynamic quality of solvents in relation to TPU, SAN, and their blended compositions, the numerical values of the intrinsic viscosity of the polymer solutions \([\eta]\) and Huggins constant were determined. The intrinsic viscosity determines the behaviour of isolated macromolecules and is a measure of the energy loss due to friction of isolated macromolecules against the solution during their rotation and back-and-forth movement in the solution [5]. It is believed [3, 5, 10] that differences in the values of the intrinsic viscosity of solutions of flexible-chain polymers are due to the fact that in different solvents the molecular coils have dissimilar sizes. In thermodynamically “good” solvents, the coils swell more than in “poor” solvents, and consequently in “good” solvents the intrinsic viscosity of the solutions is higher.

According to the obtained data (Figure 1), and guided by basic notions of the physical chemistry of polymers, it was established that, for thermoplastic polyurethane and the styrene-acrylonitrile copolymer, \(N,N\)-dimethylformamide and tetrahydrofuran are thermodynamically “good” solvents. For each polymer, the solvents can be placed in the following order of decreasing thermodynamic affinity: DMF (THF) > MEK > EA > A. A similar pattern is observed in the entire range of ratios of the TPU/SAN binary blends.

It has been reported [14, 15] that polyurethane thermoplastic elastomers and styrene-acrylonitrile copolymers, at certain ratios of the polymers, demonstrate the formation of a single-phase system. To assess the influence of the solvent on the compatibility of the given polymers, films formed from solutions of the polymers in ethyl acetate, methyl ethyl ketone, acetone, and tetrahydrofuran were investigated by methods of differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The results of studying the phase composition of polymer blends by determining a number of melting temperatures and relaxation transitions according to data of DSC curves and the temperature dependence of the slope tangent of mechanical losses are presented in Table 1 and in Figure 2.
The DSC curves for the initial polyurethane thermoplastic elastomer and for films produced from a solution of TPU in different solvents are characterised by the presence of a peak corresponding to the endothermic process associated with melting of the crystalline phase. The phase transition corresponding to the glass transition temperature of SAN and “soft” segments of TPU is represented by an S-shaped section of the DSC curve. It must be pointed out that, for SAN specimens formed from solutions, the values of the glass transition temperature are displaced considerably towards lower values by comparison with the initial polymer (Table 1).

Returning to the results of investigating the thermodynamic quality of the solvent, it is difficult, on the basis of studying weak solutions, to draw clear conclusions concerning the influence of the nature of polymer-solvent interaction. Prominence must be given to the fact that the use of a thermodynamically “poor” solvent - acetone - ensures the greatest range of polymer ratios, when the mutual solubility of polymers TPU/SAN can be questioned. Microphase separation and the formation of a two-phase structure are observed in the case of using ethyl acetate as the solvent, whereas for films formed from solutions in acetone, methyl ethyl ketone, and tetrahydrofuran, depending on the polymer ratio, a blended composite is formed that has a single temperature transition corresponding to melting of the crystalline phase (Figure 2).

The greatest degree of association of macromolecules in solution is observed in a “poor” solvent. If in this case another polymer is added, then the affinity for the solvent will be even lower [14]. On the other hand, the higher the degree of association in solution, the more ordered are the associates in the films obtained. This leads to an increase in the degree of ordering of the crystals and to an increase in the crystallisation temperature, which is observed with a TPU:SAN ratio of 10:90 wt% (solvents EA and A). In a “good” solvent – tetrahydrofuran— the blend does not react to the presence of SAN.

The glass transition temperature $T_g$ is absent when the polymers do not manage to separate into layers during film formation. This depends both on the intensity of interaction between the polymer and solvent, as can be seen in the case of the use of ethyl acetate, and on the rate of evaporation of the solvent - acetone has the greatest volatility, and the polymer blend does not manage to separate out. The existence and the magnitude of $T_g$ indicate the degree of separation into layers: high values of $T_g$ for blends with a TPU:SAN ratio of 50:50 and 30:70 wt% (solvents EA and MEK) indicate that complete separation into layers has taken place, while reduced values of the given property are observed where separation is incomplete.

The presence of a crystalline part, which is observed for all polymer ratios, is due to the fact that the thermodynamics “governs crystallisation”, while normal separation into layers depends on the kinetics of film formation during removal of the solvent [10].

Polar groups with a high cohesion energy, present in considerable quantities in TPU, are capable of forming strong intermolecular, in particular hydrogen bonds.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>PU</th>
<th>TPU:SAN ratio (wt%)</th>
<th>SAN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>80:20</td>
<td>50:50</td>
<td>30:70</td>
</tr>
<tr>
<td>Tm</td>
<td>$T_g$</td>
<td>Tm</td>
<td>$T_g$</td>
</tr>
<tr>
<td>EA</td>
<td>53</td>
<td>–38</td>
<td>51</td>
</tr>
<tr>
<td>A</td>
<td>54</td>
<td>–34</td>
<td>48</td>
</tr>
<tr>
<td>MEK</td>
<td>50</td>
<td>–35</td>
<td>58</td>
</tr>
<tr>
<td>THF</td>
<td>60</td>
<td>–41</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>–48</td>
<td>54</td>
</tr>
</tbody>
</table>

* $T_g$ is the glass transition temperature; $T_m$ is the melting temperature of the crystalline phase.

**For film specimens obtained by pressing of TPU: $T_m = 56°C, T_g = 46°C$; SAN: $T_g = 116°C$.

**Grey shading denotes polymer ratios for which compatibility is observed.

**Italic font denotes data obtained by the DMA method.

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Polar groups with a high cohesion energy, present in considerable quantities in TPU, are capable of forming strong intermolecular, in particular hydrogen bonds.
It is assumed [16, 17] that a weighty role in the mutual solubility of TPU and SAN is played by >NH--C- hydrogen bonds formed between nitrile groups of SAN and >NH urethane groups.

In a study of the IR spectra of films formed from solutions of individual polymers and their blends in ethyl acetate and tetrahydrofuran, the focus was on analysis of the absorption bands in the 1700 and 3330 cm$^{-1}$ regions. For films based on TPU, a low-frequency 1700 cm$^{-1}$ band was revealed, belonging to >C=O groups of the urethane bond, bound by hydrogen bonds, and a high-frequency 1730 cm$^{-1}$ band corresponding to “free” ester carbonyl groups, which is consistent with data of earlier studies [16, 17]. It was established that, for all TPU:SAN ratios with which a blended composite is formed that has a single temperature transition corresponding to melting of the crystalline phase (Table 1), the intensity of the C=O band at 1700 cm$^{-1}$ decreases, together with increase in the contribution to the high-frequency carbonyl band, with the >NH groups nearly all being bound by hydrogen bonds, demonstrating a broad band at 3330 cm$^{-1}$ (the band of the free unbound N-H groups should have the form of a sharp peak at about 3440 cm$^{-1}$).

The influence of the solvent on the structure of the studied composites was also studied by EPR spectroscopy. The correlation time $\tau$ characterises the rotational mobility of the probe, and consequently the segmental mobility of the chains in the amorphous phase of the polymer (composite). The concentration of radical in the film will mainly be determined by the density of the amorphous phase. According to the data presented in Figure 3 it can be seen that, with increase in the proportion of polyurethane thermoplastic elastomer, the influence of the nature of the solvent on the radical concentration increases. On the whole, based on the result obtained, it can be concluded that the density of the amorphous phase of TPU is considerably lower than in SAN.

Data on the molecular mobility in the studied blended composites are presented in Figure 4. From the figure it can be seen that the lowest values of the correlation times are observed in composites formed from solutions in THF, which indicates that in these specimens the highest molecular mobility is in the amorphous regions. The rigidity of the amorphous regions in all studied polymers and polymer composites increases with deterioration in the thermodynamic quality of the solvents in the order THF < MEK < EA < A (Figure 4). This is in good agreement with the known fact [2, 10] that increased interaction between combined polymers is observed in solutions and in films produced from solutions with the use of a “poor” solvent, in the present case acetone. The correlation times in PU and SAN, just like the concentration of radical, differ greatly (by two orders of magnitude). These data indicate phase inversion in the region of 50% PU and 50% SAN. The fact that displacement of the inflection point is observed in the case of solvents THF and MEK can be attributed to the fact that the radical concentration in amorphous regions of PU is much greater than in SAN, and “delay” of phase inversion occurs.

In earlier studies it was shown that the solvent is a “powerful” formulation factor controlling the processing of polymer solutions [1-9]. The obtained data using DSC and DMA methods demonstrated that, in spite of the practically complete removal of solvent during film formation, the choice of solvent ensures a range of TPU and SAN ratios with which a synergistic effect is observed, manifested by the formation of a single-phase system.

Summing up and analysing data concerning study of the thermodynamic quality of solvents in relation to a wide range of polymers [2, 3, 5, 7, 9, 12], the following should be noted. TPU/SAN systems (Figure 1) and nitrile butadiene rubber/chlorinated polyvinyl chloride [2, 7], in the entire range of their ratios, are characterised by an identical order of solvents of different chemical classes from the viewpoint of decrease in their thermodynamic quality, i.e. the order of transition from a “good” solvent to a “poor” solvent. This makes it possible to put forward the hypothesis that the general trends of change in the quality of the same solvents in relation to individual polymers and their blends as a consequence of the realisation of
the particular types of intermolecular interaction of which macromolecules of polymers are capable, depending on the chemical structure of the solvent, provide a basis for predicting their compatibility in blends.

REFERENCES


Received 1.4.2013