

PREDICTION OF POLYMER BLENDS STRUCTURE

NAPOVEDOVANJE STRUKTURE MEŠANIC POLIMEROV

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Many everyday engineering applications of polymers depend on their structure-property relationship, which strongly influences polymer processability. In order to obtain a satisfactory understanding of polymers' behavior their structure should be investigated and correlated with their properties. That is particularly in the case of complicated polymer systems, e.g. block copolymers, polymer blends or compatibilized polymer blends, very difficult and time-consuming procedure.

In the present study we have shown how investigations of rheological properties can be used directly for predicting the structure of polymer blends. In spite of the fact that polymer blends are thermo-rheologically complex materials, master curves of the mechanical response were constructed. It was shown that mechanical spectroscopy might be used as a supplementary tool for predicting structure, even in such complicated polymer systems as polymer blends.

Key words: polymers, structure, rheological properties

Vsakodnevna uporaba polimerov je odvisna od medsebojnega vpliva njihove strukture in lastnosti, kar močno vpliva na predelovalne lastnosti polimerov. Da bi razumeli vedenje polimerov je treba poznati njihovo strukturo in jo primerjati z njihovimi lastnostmi. To je posebej v primeru zapletenih polimernih sistemov, kot so blokkopolimeri, mešanice polimerov ali kompatibilizirane mešanice polimerov, zahteven in dolgotrajen proces.

V naših raziskavah smo pokazali, kako lahko rezultate reoloških raziskav direktno uporabimo za napovedovanje strukture mešanic polimerov. Kljub dejstvu, da so mešanice polimerov termoreološko kompleksni materiali, smo narisali t. i. sestavljene krivulje mehanskega odziva. Ugotovili smo, da lahko mehansko spektroskopijo uporabimo kot dodatno orodje za napovedovanje strukture celo v tako zapletenih polimernih sistemih, kot so mešanice polimerov.

Ključne besede: polimeri, struktura, reološke lastnosti

1 INTRODUCTION

Polyurethanes are an important class of polymers that are used in fibers, elastomers, foams, coatings and plastics. In general, they lack thermal flexibility and stability, what consequently cause poor mechanical properties over a broad temperature range. By blending thermoplastic polyurethane (TPU) with styrene/acrylonitrile (SAN) many different properties can be achieved because of the different structures of polyurethanes (hard and soft segment character and amount, domain separation, etc.) with different SAN copolymers (weight % of AN, different distributions of styrene and AN). A comparison of the advantages and disadvantages of TPU and SAN, suggests that TPU/SAN blends could be promising materials with a broad technological potential. They have, so far, not been used commercially due to their very complex structure and incompatibility. One possible approach for achieving better compatibility is to use compatibilizers. In spite of numerous research activities in the field of compatibilization of different polymer pairs, the compatibilized TPU/SAN blends were not studied in details until now^{1,2}.

2 EXPERIMENTAL

2.1 Materials

Commercial TPU with polyester soft segments and SAN with 20 wt.% of acrylonitrile, were used as the blend's basic components. The materials were supplied by BASF, Ludwigshafen, Germany. The homopolymers and block copolymers with a well-defined structure which were used as possible compatibilizers were synthesized via living anionic polymerization. The compatibilizer's characteristics, determined by size-exclusion chromatography (SEC) and proton nuclear magnetic resonance (¹H-NMR), are summarized in **Table 1**. Compatibilized and non-compatibilized TPU/SAN 25/75 blends were prepared from a melt at 210 °C, using a co-rotating twin-screw mixer with conical screws, developed by the TU Eindhoven, Netherlands.

2.2 Characterization techniques

Ultra-thin sections of blends were cut at -60 °C with a Reichert cryoultramicrotome using a diamond knife. All samples were stained with a 4 wt.% aqueous solution of phosphotungstic acid. Electron micrographs were obtained with a CEM 902 Zeiss transmission electron microscope (TEM) using an accelerating voltage of 80 kV.

The Rheometric Dynamic Stress Rheometer (SR-500) is a stress-controlled rheometer, which was used to characterize the rheological properties of the polymer blends. Isothermal frequency sweeps were recorded between 130 and 220 °C in steps of 10 °C, in order to obtain master curves. A further increase in the temperature was impossible because of the samples' thermal instability. The frequency was varied from 100 to 10⁻² rad/s. The region of linear viscoelastic behavior was determined using stress sweeps. Master curves were constructed using the Rheometric RheCurve software, which determines shift factors empirically. The program calculates the shift factors that give the best superposition of the data points when they are multiplied by the frequency of each measurement made at a given temperature.

Table 1: Molecular properties of synthesized polymers.
Tabela 1: Molekularne lastnosti sintetiziranih polimerov

Compatibilizer's denotation	Structure	M _w · 10 ^{-3 a)}	M _w /M _n ^{a)}	wt.% of A block ^{b)}
		(g/mol)		
C1a	PCI	104	1.31	-
C1b	PCI	87	1.24	-
C1c	PCI	49	1.40	-
C2	PS-b-PCI	65	1.25	30
	PS-b-PMMA	78	1.16	24
C3	PB-b-PMMA	105	1.07	29
	PI-b-PCI	137	1.18	65

a) Obtained by SEC for C2, A-block = PS

b) Obtained by ¹H NMR for C3, A-block = PB or PI

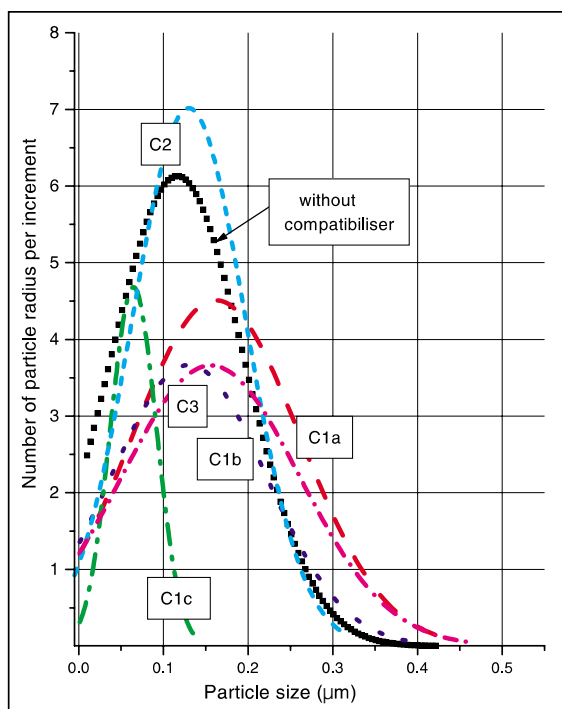


Figure 1: Normal distribution curves of particle radius
Slika 1: Krivulje normalne porazdelitve premera delcev

3 RESULTS AND DISCUSSION

The effect of the compatibilizers on the morphology of the TPU/SAN 25/75 blends was investigated on the basis of the distribution of domain sizes³. The area of each particle obtained from corresponding TEM micrographs was measured and the particle radius calculated assuming that all particle images are circles. The normal distribution curves obtained from the corresponding histograms are shown in **Figure 1**. Because the curves are not normalized, only the curve widths are comparable indicators of dispersed domain size and the curve heights have to be neglected. The influence of the molecular weight of C1x (PCIs with different M_w) on the blends' morphology can be clearly seen. The increase of the size of the dispersed TPU domains indicates that C1a (PCI with the highest M_w) probably causes coalescence, while the addition of C1c (PCI with the lowest M_w) reduces the size of the domains. Moreover, a narrower distribution of domain sizes was obtained with the addition of C1c. The broader distributions show that the size of the dispersed TPU domains increases in blends compatibilized with C2 and C3, when compared with the non-compatibilized blend. This indicates that C2 and C3 do not stabilize the morphology against coalescence. The TEM micrograph of the TPU/SAN blend compatibilized with C1c is shown in **Figure 2**.

In spite of many contradictory opinions about the possibility of using the time-temperature superposition (TTS) principle to generate master curves for thermo-rheologically complex materials^{4,5} and the fact that immiscible polymer blends are not, strictly speaking, thermo-rheologically simple materials, we applied TTS for non-compatibilized and compatibilized TPU/SAN 25/75 blends. The behavior of these blends

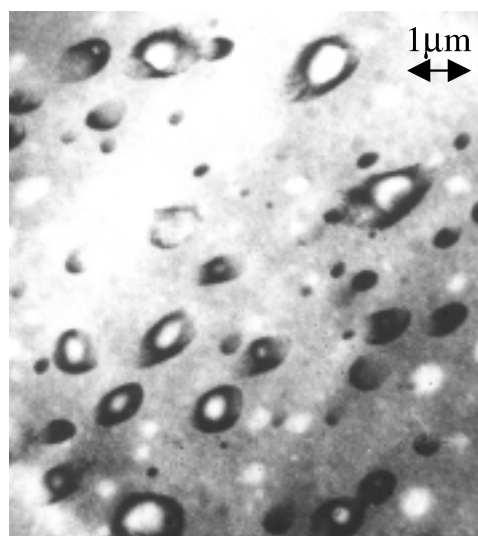


Figure 2: TEM micrograph of TPU/SAN 25/75 blend compatibilized with 5 wt.% of C1c

Slika 2: TEM-posnetek mešanice TPU/SAN 25/75, kompatibilizirane s 5 mas.% C1c

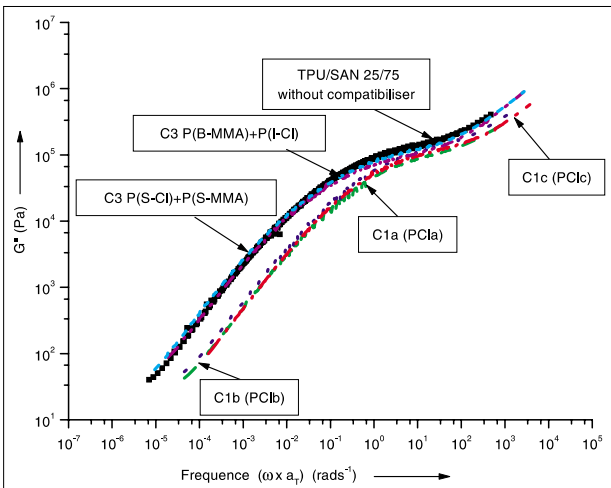


Figure 3: Master curves of the loss shear modulus (G'') of TPU/SAN 25/75 blends as a function of frequency ($T_r = 150\text{ }^\circ\text{C}$)
Slika 3: Sestavljene krivulje dinamskega strižnega modula izgub (G'') mešanic TPU/SAN 25/75 v odvisnosti od frekvence ($T_r = 150\text{ }^\circ\text{C}$)

was expected to be complex and dominated by the SAN matrix.

We found that the TPU/SAN 25/75 blends showed a rheological behavior, that is between the behavior of the pure components³. However, the influence of SAN predominates since it builds the matrix phase⁶. At higher frequencies the blends behave similar to SAN, but at the lower frequencies the influence of the dispersed TPU phase was observed, and as a consequence, the dynamics data do not follow well-known patterns such as Arrhenius or WLF. A dependence of approximately $G \propto \omega^{0.5}$ was found, which is typical for phase-separated polymers^{3,7,8}. The transition from the elastic plateau to the flow region is broad, which is typical for polymers with a broad molecular-weight distribution⁹.

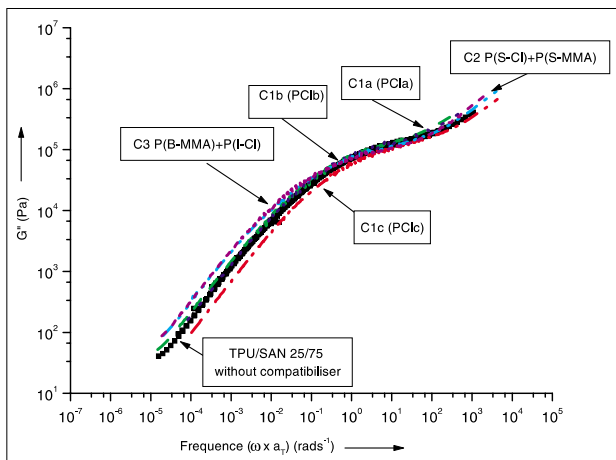


Figure 4: Master curves of the loss shear modulus (G'') of TPU/SAN 25/75 blends as a function of frequency ($T_r = T_g \text{ SAN} + 50\text{ }^\circ\text{C}$)
Slika 4: Sestavljene krivulje dinamskega strižnega modula izgub (G'') mešanic TPU/SAN 25/75 v odvisnosti od frekvence ($T_r = T_g \text{ SAN} + 50\text{ }^\circ\text{C}$)

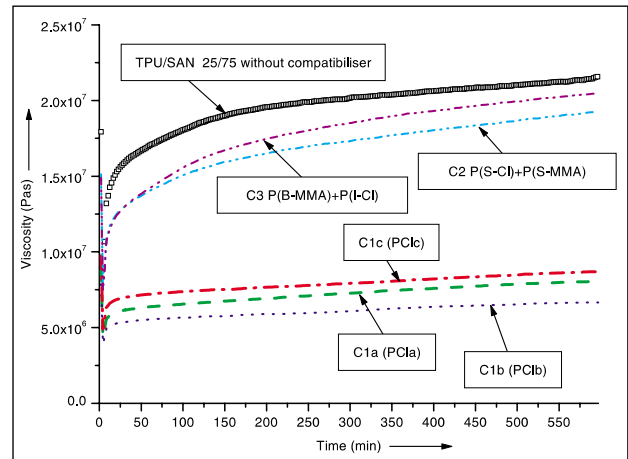


Figure 5: Viscosity of non-compatibilized and compatibilized TPU/SAN 25/75 blends during a creep period of 600 min
Slika 5: Viskoznost nekompatibiliziranih in kompatibiliziranih mešanic TPU/SAN 25/75 med strižno obremenitvijo 600 min

Figure 3 shows the effect of the compatibilizers on the dynamic moduli of the TPU/SAN 25/75 blends, with $150\text{ }^\circ\text{C}$ taken as the reference temperature for all master curves. At high frequencies there are only small differences between non-compatibilized and compatibilized TPU/SAN 25/75 blends. Larger changes in the modulus values are observed for blends compatibilized with C1x. Furthermore, the addition of the PCI homopolymers shifts the flow region to higher frequencies, in comparison with the non-compatibilized blend and the blends compatibilized with C2 and C3. A shift to higher frequencies corresponds to lower relaxation times and means that for a given temperature, blends compatibilized with the C1x will flow within a shorter period. The shift of the flow region to higher frequencies can be a consequence of changes in the morphology of the blend or of changes in the T_g of the phases, mainly of the phase with the highest T_g .

In order to eliminate the influence of the T_g of the SAN-rich phase on the terminal flow region of the blends, master curves with $T_r = T_g(\text{SAN-rich phase}) + 50\text{ }^\circ\text{C}$ were also constructed from the experimental data (**Figure 4**). In this case, we can clearly see that only the addition of C1c shifts the flow region to higher frequencies, while the addition of the other compatibilizers shifts the flow region to even lower frequencies, indicating that only the blend compatibilized with C1c should have smaller domains of the dispersed phase. This is in agreement with the results of the morphological investigations, which clearly show that the size of TPU-rich-phase domains for the blend compatibilized with C1c is much smaller than the size of the domains of the other blends.

The viscosity (η) versus time curves (**Figure 5**) of the molten non-compatibilized and compatibilized TPU/SAN blends were obtained from strain versus time curves during a creep period of 600 min at $140\text{ }^\circ\text{C}$. The

decrease of η was ascribed to the share of PCI in the compatibilizers, which can be related to the decrease of the T_g of the SAN-rich phase in these blends, as found in the investigations of thermal and thermo-mechanical properties^{6,10}. To obtain some additional information about behavior in the steady state, creep measurements should also be performed at the temperatures with a constant distance to the higher T_g of the blend.

4 FINAL REMARKS

The master curves of the TPU/SAN 25/75 blends show a rheological behavior between that of their pure components. However, the SAN, which builds the matrix phase, has a stronger influence. When a constant temperature is chosen as the reference temperature, the flow region of all the compatibilized blends is shifted to higher frequencies. When a temperature with a constant distance to the highest T_g of the blend is chosen as a reference temperature, only the flow region of the blend compatibilized with C1c is shifted to higher frequencies. Taking into account that a shift to higher frequencies is an indication of a finer morphology and that only with C1c were smaller domain sizes found by TEM, it can be concluded that the differences in T_g have to be taken into account when constructing master curves and interpreting results.

The TPU/SAN blends compatibilized with C2 and C3 (a mixture of two block copolymers) are too complicated to be adequately understood. Nevertheless, our results show that poly(ϵ -caprolactone)s, with an appropriate M_w , improve the compatibility of TPU/SAN blends (smaller domains). A particular advantage of using PCI as a compatibilizer for TPU/SAN blends is that this homopolymer can be more easily prepared on a commercial scale, principally if its synthesis is compared to the much more troublesome synthesis of

high-molecular-weight block copolymers, that are normally used as compatibilizers.

It was also shown that mechanical spectroscopy might be used as a supplementary tool for the structure prediction of complex polymer systems. However, rheological investigations can be used for the identification of compatibilization efficiency.

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