



Relaxation properties of polyoxymethylene and ethylene–octene copolymer blend in solid and melt states

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Abstract. Rheological properties of polyoxymethylene (POM) and ethylene–octene copolymer (EOC) in solid and melt states were investigated. Blends were prepared with a twin screw extruder at broad component wt-to-wt ratios (10, 30, 50, 70, 90 wt% of EOC). The morphology as well as calorimetric, rheological, and elastic properties of the blends were studied. The investigation showed that POM/EOC blends were heterogeneous in nature and had a broad phase transition region between 30 and 70 wt% of POM. Because during processing droplet breakup is enhanced for EOC-rich systems, respective blends show “better” morphology with smaller particle sizes. It was, however, observed that rheological and dynamic characteristics (such as storage E' and loss E'' modules as well as shear elastic G' and viscous G'' modules) were highly influenced by intrinsic incompatibility of POM and EOC. Besides, also the crystallization specifics of the investigated blends influenced their E' and E'' .

Key words: polyoxymethylene, ethylene–octene copolymer, blends, rheological properties, dynamic properties.

INTRODUCTION

Polyoxymethylene (POM) is one of the most important engineering polymers. It provides high surface hardness, low wear and friction, and high resistance to chemicals such as alcohols, aldehydes, esters, and glycols. Potential applications of POM are medical devices, automotive components, water and gas tubing systems, household equipment, etc. At the same time POM modification with other thermoplastics, elastomers [1,2], and inorganic fillers [3–6] can increase the impact strength, thermal resistance, and other properties of the polymer. These new blends can be used in different areas of economy: packing, production of electronic devices, etc. [7,8].

In this study ethylene–octene copolymer (EOC) was used as a high-molecular modifier of POM. EOC is a new class of thermoplastic elastomers. It provides high superelasticity and impact strength. Like other elastomers this

polymer is widely used in various industries where tough superelastic materials are required, for example, the manufacture of gaskets. In blends EOC is most often used for increasing the impact strength of the material [9]. There are numerous literature sources that demonstrate the effectiveness of POM modification with other elastomers. For example, POM modification with acrylonitrile–butadiene elastomer improves processability [1], nitrile rubber additives improve yielding behaviour and increase oil resistance at elevated temperatures [2], addition of polyurethane and CaCO_3 provide well-balanced mechanical properties [6].

Structural and mechanical properties of POM/EOC blends were addressed in our previous work [10]. In this publication we mainly focus on the structure and rheology of POM/EOC blends. These parameters determine the ease of processing polymer materials and should be viewed in combination with exploitation properties.

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EXPERIMENTAL

The polyoxymethylene (POM) and ethylene–octene copolymer (EOC) used in this study were commercial products. POM (*Kocetal K300*) has melt flow index (MFI) 9 g/10 min, density (ρ) 1.41 g/cm³, melt temperature 439 K. EOC with 38% alpha octene content (*Dow Engage 8200*) has MFI 5 g/10 min, density 0.87 g/cm³, maximum melt temperature 333 K.

Blends were prepared with a twin screw extruder *Thermo PRISM TSE 16 TC* at broad component wt-to-wt ratios (10, 30, 50, 70, 90 wt% of EOC). Temperatures in the extruder processing zones were 443, 448, 450, 450, and 453 K (die); screw rotation speed was 70 rpm. Blends were extruded twice, as such an approach ensured better mixing, due to which the blends have lower void content as it was shown in our previous work [10].

Rheological properties of POM/EOC blends were investigated by means of a melt flow indexer and rotation viscometer. Melt flow index was determined according to LVS EN ISO 1133 by using an *IIIPT-AM* melt flow indexer. Experiments were performed at the temperature of 463 K and load of 2.16 kg with a capillary having a length of 8 mm and orifice diameter of 2.095 mm. Viscosity curves of neat polymers and blends were measured with a *REOLOGICA StressTech NOVA* plate to plate viscometer in the linear visco-elasticity region (LVER) and frequency sweep mode (FSM).

The relaxation behaviour of POM/EOC blends in solid state was investigated by means of a *TA Instruments Q800* dynamic mechanic thermal analyser. Experiments were performed in single cantilever mode at a frequency of 1 Hz.

Structural properties of POM/EOC blends were investigated by using a *Mettler Toledo DSC1/200W* differential scanning calorimeter (DSC). All measurements were made under N₂ flow; samples (~10 mg) were heated from 173 up to 473 K at a scanning rate of 283 K/min.

The morphology of POM/EOC blends was studied with an *EOS CamScan MV2300* scanning electron microscope equipped with an *EDX* energy dispersive X-ray spectroscopy system. Fracture surfaces of the test specimens, broken in liquid nitrogen, were investigated at 20 kV voltage and $\times 1000$ magnification.

RESULTS AND DISCUSSION

Experimental and theoretical melt indices as functions of the EOC content are shown in Fig. 1. Experimental melt flow index values were determined at 463 K under 2.16 kg load, while theoretical melt indices were calculated according to the rule of mixtures. The experimental melt flow index values of the investigated blends

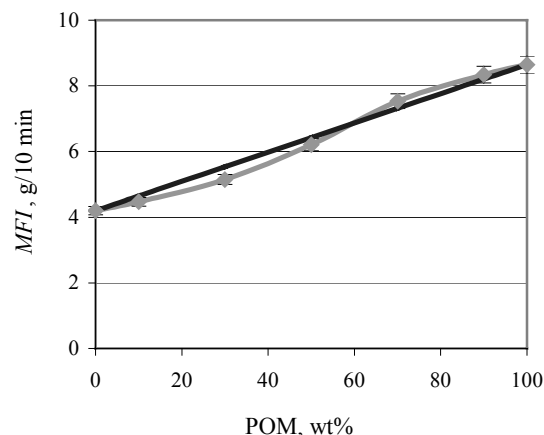


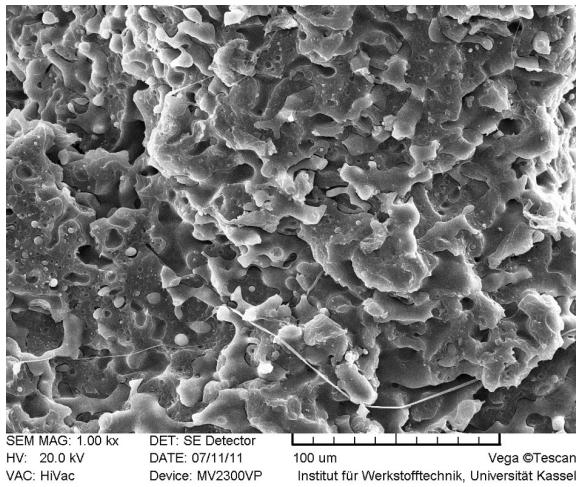
Fig. 1. Melt flow index *MFI* of POM/EOC blends as a function of POM weight content at 463 K and 2.16 kg.

were higher than theoretical in the POM content interval 60–100 wt%. In the POM content interval from 0 to 60 wt% the opposite situation was observed: experimental melt flow index values were lower than theoretical. Consequently, viscosities for polymer blends containing up to 60 wt% POM were higher than theoretical, while those with POM content above 60 wt% were lower than theoretical. This is a traditional situation for heterogeneous binary polymer blends: up to ~30 wt% POM content it is dispersed in the elastomer matrix, while above 70 wt% POM elastomer is dispersed in the POM matrix. Thus, POM/EOC blends are characterized by a broad phase transition region between 30 and 70 wt% POM.

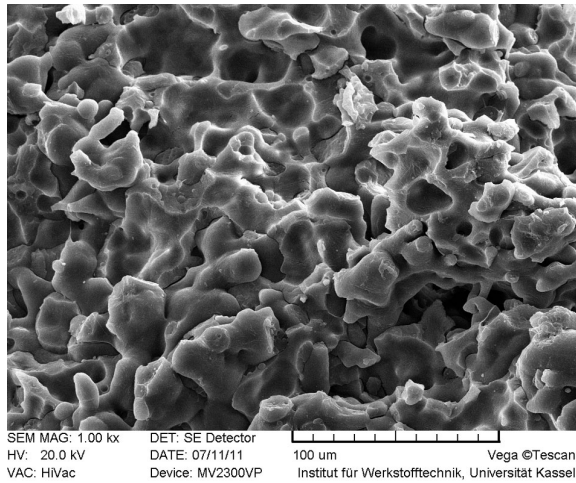
The observed experimental viscosity deviations from theoretical values may indicate also interaction of blend components. As stated by Utracki [11], positive viscosity deviation is explained by certain interaction between the components of the system at low shear rate. Negative viscosity deviation, in turn, is usually explained by low interaction between components, which is most often due to low compatibility. Besides, positive and negative viscosity deviations are also associated with viscosities of the blend components, i.e., low viscosity of a matrix component is usually associated with negative viscosity deviations, as it was observed also in our case. Viscosity ratio, which is defined as the ratio of the viscosity of the dispersed phase to that of the matrix, has been shown to be one of the most critical factors controlling the morphology of multiphase systems [12].

In the case of the investigated systems the viscosity ratio for the POM matrix blends was ~2.25 and for EOC matrix blends, ~0.4. Consequently, droplet breakup will be enhanced for the EOC matrix blends and hampered for the POM matrix blends. To prove this statement, SEM micrographs of POM/EOC blends are shown in Fig. 2. As can be seen, EOC matrix blends are charac-

(a)



(b)



(c)

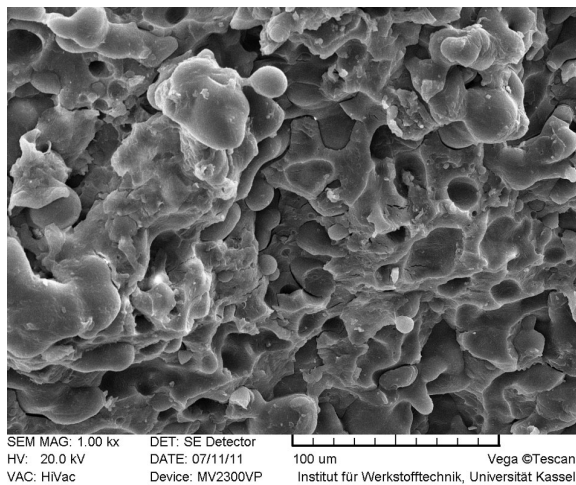


Fig. 2. Scanning electron micrographs of POM/EOC blends: (a) POM30/EOC, (b) POM50/EOC, and (c) POM70/EOC (in wt%).

terized by smaller sizes of the dispersed phase particles than those observed in the POM matrix blends. Evidently, higher viscosity of the EOC matrix enhances droplet breakup because of more efficient shear stress transfer towards the dispersed phase and a somewhat reduced coalescence probability. Usually smaller particle sizes along with better distribution of the minor phase in the polymer matrix are associated also with better interaction between the components. It should, however, be mentioned that for all the investigated blends smooth rupture surfaces were observed, testifying to their incompatibility, especially in the case of the POM50/EOC blend (Fig. 2b).

To characterize viscosities of POM/EOC blends in broader shear rate regions, measurements in LVER at 1 Hz frequency were initially made. Results of these measurements are shown in Fig. 3. As it was already expected from the melt flow index tests, the viscosity of EOC was higher than that of POM. Viscosity curves of the investigated blends of POM/EOC mostly fall outside the region covered by the viscosity curves of neat polymers. As shown in Fig. 3, viscosities of the investigated blends as functions of blend content change by

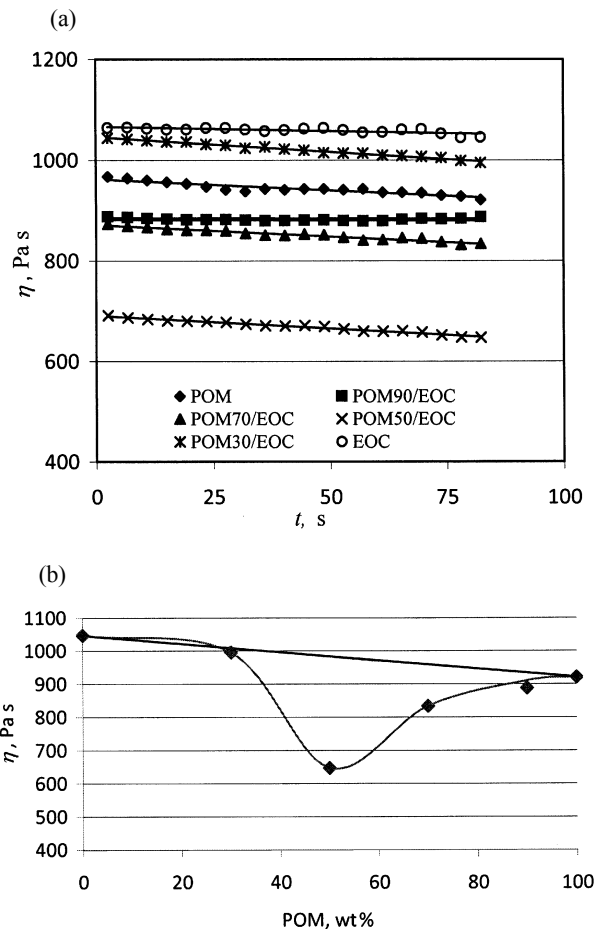


Fig. 3. Dynamic viscosity η of POM/EOC blends as a function of time (a) and of POM weight content (b).

showing expressed minima corresponding to the phase transition region. Decreased viscosities of the blends in respect to POM and EOC are evidently connected with poor compatibility. In addition, time sweep experiments showed that at increasing shear time the viscosities of the blends fell faster than those of the neat components.

Frequency dependence of the rheological characteristics of the blends of POM/EOC is shown in Fig. 4. It is important to mention that viscosities of POM and EOC approach each other when frequency increases. Thus, at a frequency of 40 Hz (~250 rad/s), common for many traditional polymer processing methods such as extrusion and blow moulding, the difference between the viscosities of POM and EOC is several times smaller than at 1 Hz. This allows assuming that from the viewpoint of rheology rather favourable conditions for mixing POM and EOC have been created and the main reason for coarse morphology is intrinsic incompatibility between the blend components, causing the viscosity curves of the investigated blends to fall out of the viscosity envelope confined by the characteristic relationships of POM and EOC. Similar trends are characteristic also of shear G' and loss G'' modules, i.e., modules of POM are greater than those of EOC, while all the blends, except for POM90/EOC, have modules lower than the neat polymers. Besides, both modules, G'' being greater than G' , increase with frequency by approaching each other, although without intersection within the measuring range. In the case of POM90/EOC blend, somewhat better interaction between the neat polymers could be expected. The strength of interaction or internal structure could be measured by the magnitude of the ratio $G''/G' = \tan \alpha$, known as damping factor (α denotes phase angle). The smaller $\tan \alpha$ (or the greater G''), the stronger is the interaction.

Comparison of dynamic viscosities η^* , modules G' and G'' , and phase angles α of the investigated POM/EOC blends as functions of frequency showed that the smallest deviations from the respective additive values were for blends with a small content of the minor phase component (Fig. 5). Consequently, for these minor phase blends better interaction between the blend components is expected. An example is the composition of POM30/EOC, which has the smallest α and the highest G'' in conjunction with the smallest sizes of the dispersed phase particles.

Relaxation properties of POM/EOC in solid state were investigated in a broad temperature range applying the DMTA technique. Storage E' and loss E'' modules and $\tan \delta$ of POM/EOC blends are shown in Fig. 6. As blends of semi-crystalline polymers are investigated, at least the following characteristic relaxation transitions are clearly observed: (1) glass transition of POM near 203 K, (2) glass transition of EOC near 223 K, and (3) crystalline phase perfection of POM near 363 K. As

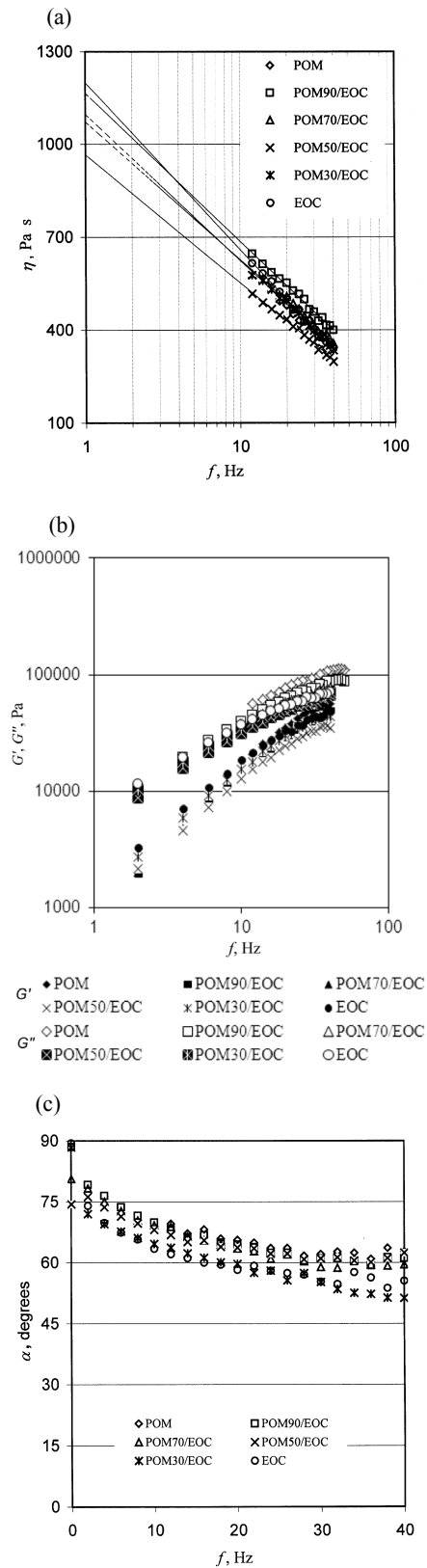


Fig. 4. Dynamic viscosity η^* (a), shear elastic G' and viscous G'' modules (b), and phase angle α (c) of POM/EOC blends as functions of frequency.

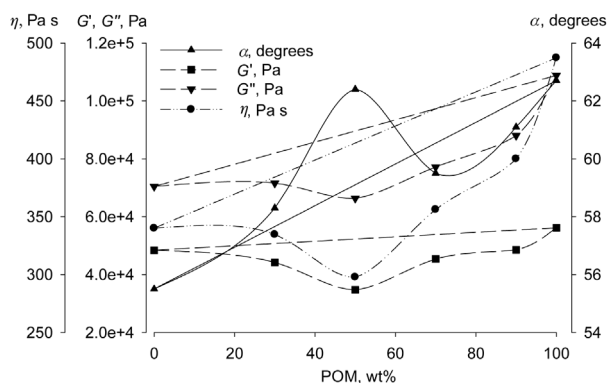


Fig. 5. Dynamic viscosity η^* (a), shear elastic G' and viscous G'' modules (b), and phase angle α (c), measured at frequency 40 Hz and temperature 463 K, as functions of POM weight content.

it was expected, modules of the investigated blends increased with rising POM content. Especially in “ $\tan \delta$ – T ” relationships it is evident that blends with similar POM and EOC contents, especially those of POM50 and EOC, have least compatibility, showing two distinguishable glass transition temperatures of neat polymers. However, if glass transition temperatures characteristic of neat polymers were approaching each other to some extent in the case of POM70/EOC, in the case of POM50/EOC such behaviour was not observed. This again confirms that the composition with 50 wt% of EOC has least compatibility. If to compare the elastic modulus of the investigated blends at 298 K (Fig. 7), it can be seen that experimental data are considerably lower than those calculated according to the rule of mixtures, especially for POM lean blends. Considering that POM lean blends have smaller dispersed particle sizes, it is evident that apart from incompatibility, there are other reasons for lower values of elastic modulus of the blends, one of such possible reasons being changes in the crystallinity of the blends.

The influence of crystallinity was verified in differential scanning measurements. It is documented that the used EOC with the octene group content of 38% exhibits two melting peaks, the lower one attributed to the melting of hexyl branches and the higher to the melting of the main chain crystalline segments [13]. Consequently, in DSC thermograms of POM/EOC blends three melting peaks could be distinguished as demonstrated in Fig. 8a. As can be seen, the blend components influence each other's crystallization. With the addition of EOC to POM, the melting peak temperature of the matrix component rises. In the case of EOC-rich blends, addition of POM causes an increase of the higher melting peak temperature of the elastomer, while its lower melting peak temperature remains practically unaffected. As to crystallinity degrees, it can be observed that the components hinder each other's

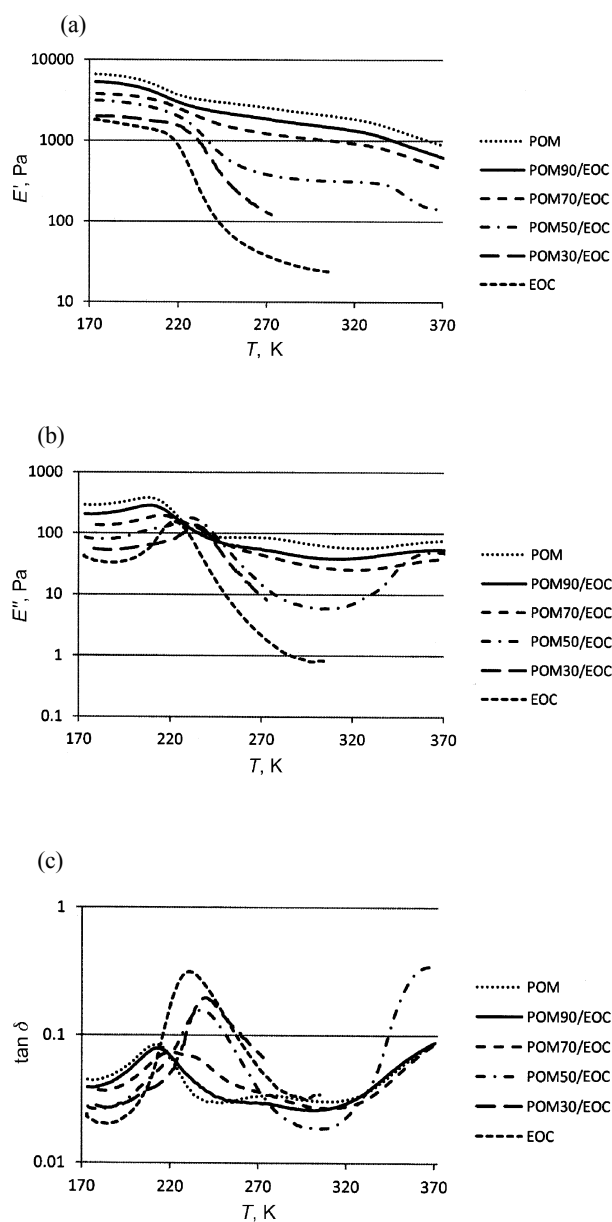


Fig. 6. Storage E' (a) and loss E'' modules (b) and $\tan \delta$ (c) of POM/EOC blends as functions of temperature.

crystallinity degree. It is evident that the effect of POM on the EOC crystallization behaviour is greater than the opposite effect. Besides, the greatest deviations of experimentally detected total crystallinity degrees from respective additive values are for blends with a small POM wt% content, as it is clearly demonstrated in Fig. 9. These reduced crystallinity degrees of the blends in respect to neat polymers could also explain some negative deviations of the experimental elastic modulus values from the theoretical ones because the elastic modulus greatly depends on crystallinity.

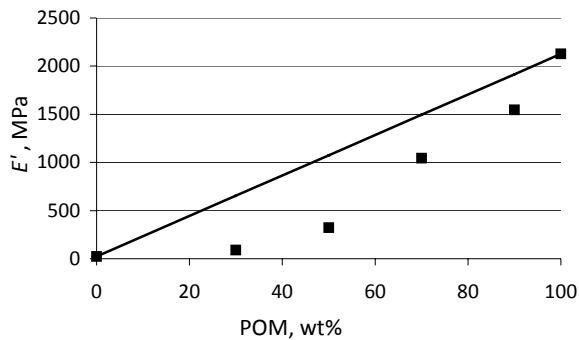


Fig. 7. Storage E' modulus of POM/EOC blends as a function of POM weight content.

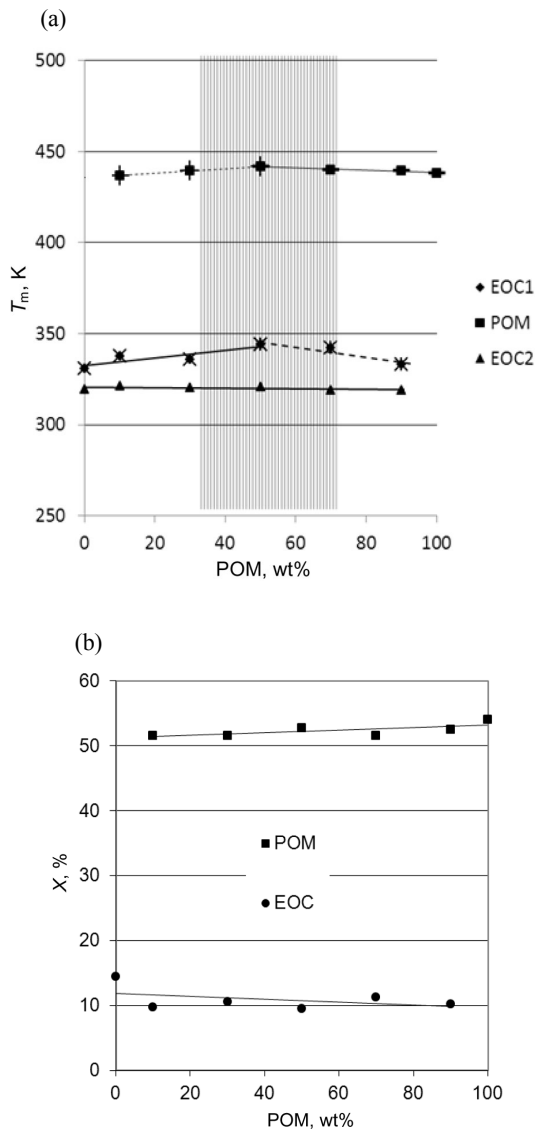


Fig. 8. Melting peak temperatures T_m (a) and crystallinity degrees X (b) of POM/EOC blends as functions of POM weight content. EOC1, melting of hexyl branches; EOC2, melting of crystalline segments of the main chain.

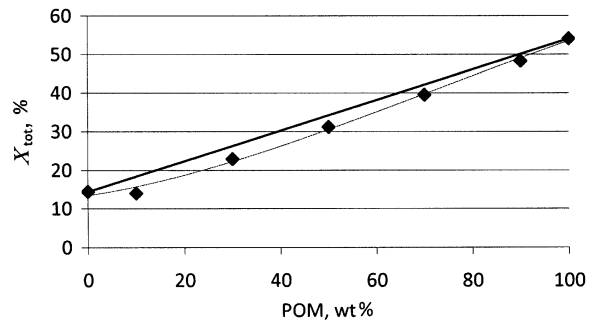


Fig. 9. Total crystallinity X_{tot} of POM/EOC blends as a function of POM weight content.

CONCLUSIONS

The relaxation behaviour of POM/EOC blends in solid and melt states was investigated. Results of the investigation testify that POM/EOC blends are heterogeneous in nature and are characterized by a broad phase transition region between 30 and 70 wt% POM. Considering that for the POM matrix blends the viscosity ratio is ~ 2.25 , while that for the EOC matrix blends it is ~ 0.4 , droplet breakup is enhanced for the EOC-rich systems. Consequently, EOC-rich blends show “better” morphology with smaller particle sizes.

Viscosities of the blends, especially of POM50/EOC, are lower than those for neat components, thus testifying on intrinsic incompatibility between POM and EOC. However, blends with smaller minor phase contents showed higher values of viscous modulus G'' and lower values of phase angle α , indicating somewhat better interaction between neat components.

Similarly, storage E' and loss E'' modules are highly influenced by incompatibility of POM and EOC. Besides, E' and E'' of the investigated blends decreased to some extent in respect to neat components due to the fact that POM and EOC hinder each other's crystallization.

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Polüoksümetüleen ja eteeni ning okteeni kopolümeeri segu relaksatsiooniomadused tahkes ja sulaolekus

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Hans-Peter Heim ja Christian Berger

Uuriti polüoksümetüleen (POM) ja eteeni ning okteeni kopolümeeri (EOC) segude reoloogilisi omadusi tahkes ja sulaolekus. Segud valmistati kaheteolise ekstruuderiga komponentide massisuhte laias vahemikus (10, 30, 50, 70, 90% EOC). Segude morfoloogia, nende kalorimeetriliste, reoloogiliste ja elastsusomaduste uurimise tulemused näitavad, et POM-i/EOC segud on olemuselt heterogeensed ning neid iseloomustab lai faasiüleminekupiirkond massisuhte vahemikus 30–70% POM. EOC-rikastel segudel on “parem” morfoloogia (väiksem osakeste suurus). Samas täheldati POM-i ja EOC molekulide kokkusobimatuse suurt mõju reoloogilistele ning dünaamilistele näitajatele (viskoossus, nihkeelastsus-, jääk- ja kaomoodul). Samuti mõjutavad uuritavate segude jääk- ja kaomoodulit kristallumise asjaolud.