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Abstract

We carried out detailed Raman structural study of melt-mixed blends of linear low-density polyethylene (PE) and isotactic polypropylene (PP). The relative content of PE in the PE/PP blends varied from 13 to 75 %. We show that Raman spectroscopy can be effectively used for a quantitative analysis of phase and conformational compositions of these blends. The changes in these compositions due to changing the content of the blend components are discussed. Also, we studied a structure of the amorphous phase of reactor blends of PE with random ethylene/1-hexene copolymer (CEH).

Introduction

It is well known that polymers are semicrystalline or fully amorphous stuffs. Their properties depend strongly on a great amount of structural characteristics (crystallite size, phase and conformational composition, etc.), and detailed structural characterization is an important task for development of new polymer materials. Traditional techniques of polymer characterization, such as X-ray diffraction analysis and differential scanning calorimetry (DSC), allow studying the crystalline phases. However, these techniques are limited in information about an amorphous phase. Thus, in order to understand relation between polymer properties and structure, the methods allowing analysis of the polymer amorphous phase are needed.

We applied successfully Raman spectroscopy for monitoring the phase and conformational composition for a wide number of polyolefin materials, among them - copolymers of propylene and ethylene with different α-olefins, and polyolefin/clay nanocomposites [1-3]. Recently we have demonstrated that the Raman bands at 1295 and 1330 cm^{-1} can be used for precise determination of mass proportion of PE to PP in PE/PP blends [4]. In this work, we developed Raman spectroscopy approaches for quantitative diagnostics of phase and conformational compositions of the blends containing PE and isotactic PP. The production of such blends is one of promising and economically effective ways to create new polymer materials, since this way does not require new production facilities [5]. Also, using the developed approaches, we investigate a structure of these blends as well as reactor blends of PE with CEH, in order to better understand the role of each component (PE, PP or CEH) in formation of the supramolecular structure of the blends.

Experimental

We used linear low-density PE (with the melting temperature 118°C) and isotactic PP (with the melting temperature 176°C) to produce the PE/PP blends. Melt-mixing of PE and PP was done during 15 min at temperature of 200°C. Relative PE content in the blends was varied from 13 to 75 wt %. The films of the PE/PP blends for the Raman experiments were fabricated by compression molding at 5×10^5 Pa and the subsequent water quenching at room temperature.

The manufacture of the reactor PE/CEH blends was described in detail in our recent paper [6]. Briefly, the nascent reactor PE/CEH blends are consisted of high-density ultrahigh-molecular-weight polyethylene (UHMW PE) and CEHs with different content of 1-hexene (10.9, 19.0, and 37.0 mole %) in the copolymers. The relative copolymer content in the reactor blends was varied from 7 to 35 wt. %. The PE/CEH blends were produced by two-step consecutive polymerization. At the first stage of the production process the homopolymerization of ethylene was carried out with the formation of high-density UHMW PE fraction with the molecular weight about 1 000 000 g/mole. At the second stage, the copolymerization of ethylene with 1-hexene was performed with the synthesis of random CEH fraction and very small amount of the di-block copolymer of PE and CEH.

The Raman setup, which we used to record the Raman spectra of both PE/PP blends and PE/CEH blends, consists of a Spectra Physics Stabilite 2018 Ar-Kr ion laser, a U1000 Jobin Yvon double monochromator, and a cooled PMT operating in the photon counting regime.
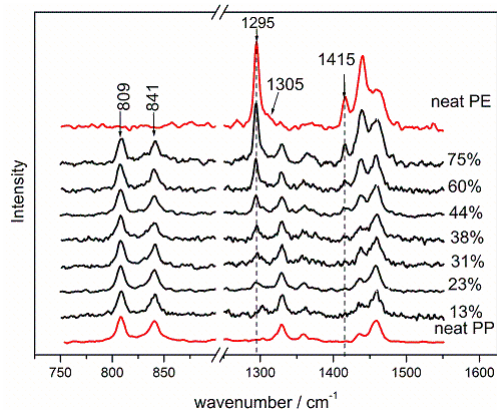

Fig. 1. Raman spectra of the melt-mixed PE/PP blends.

The spectra are measured at the 90° scattering with a spectral resolution of 5 cm^{-1}. The excitation wavelength was 488 nm. The angle between the wave vector of the excitation radiation and the normal to the surface of a sample was 45°.

We found spectral characteristics (peak positions, integral intensities, widths) by the spectra deconvolution. Form of each line was described as a weighted sum of Gaussian and Lorentzian functions. A nonlinear background fit was subtracted from the experimental spectra.

Results

Fig. 1 shows the Raman spectra of the melt-mixed PE/PP blends at different relative PE content (in wt.%). The figure also presents the spectra of the homopolymers - PE and PP, which were used for manufacturing the PE/PP blends. The spectra, except for the spectrum of neat PE, are normalized to the peak intensity of the Raman line at 809 cm^{-1}. The spectrum of neat PE is normalized to the peak intensity of the Raman band at 1295 cm^{-1}. Note, that after normalizing procedure, the peak intensity of Raman line at 809 cm^{-1} is equal to 1 in the spectra of the blends and neat PP. The neat PE spectrum was multiplied by 3, in order to save the magnitude of the spectral variations.

Fig. 2 presents the Raman spectra of three reactor PE/CEH blends (BLEND1, BLEND2, BLEND3), as well as the spectra of UHMW PE and neat CEH with 10.9 mole % of 1-hexene. The BLEND1 contains 35.8 wt. % of CEH with 10.9 mole % of 1-hexene in the CEH. The BLEND2 contains 31.5 wt. % of CEH with 37.0 mole % of 1-hexene in the CEH. The blend CEH3 contains 30.2 wt. % of CEH with 19.9 mole % of 1-hexene in the CEH.
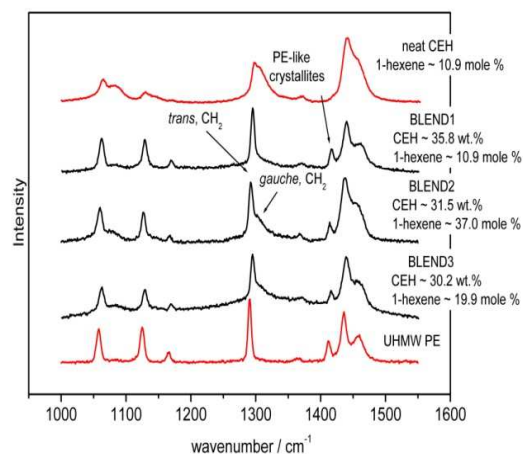

Fig. 2. Raman spectra of the reactor PE/CEH blends, UHMW PE, and neat CEH.

The spectra in Fig. 2 are normalized to the peak intensity of the Raman band at 1295 cm^{-1}.

The C-C stretching and CH_2 rocking vibrations of isotactic PP molecules are observed in spectral area from 700 to 900 cm^{-1}. The most prominent Raman lines at 809 and 841 cm^{-1} of this area are assigned to the vibrations of helical macromolecules localized in the PP crystallites and the amorphous phase, respectively [1,4,7]. Using the deconvoluntion of our experimental spectra we also found the low-intensity and broad Raman band at 830 cm^{-1}. This band corresponds to vibrations of PP non-helical macromolecules which localized in the amorphous phase [7].

The Raman lines of PE and short CH_2-chains are observed in the spectral area from 1000 to 1500 cm^{-1}. The Raman lines at 1295, 1305, and 1415 cm^{-1} are the most important for our research. For both types of the blends, these lines correspond to the deformation vibrations of CH_2 groups in CH_2-chains [2-4,8]. The Raman line at 1415 cm^{-1} is assigned to the vibrations of macromolecules localized in the orthorhombic PE (for the PE/PP blends) crystalline phase or PE-like (for the PE/CEH reactor blends) crystalline phase. Further, instead of the term "orthorhombic PE (or PE-like) crystalline phase" we use the term "orthorhombic PE crystallites". The line at 1295 cm^{-1} belongs to the vibrations of CH_2-chains in *trans*-conformation, i.e. PE crystallites and CH_2-chains in *trans* conformation, which are localized in the amorphous phase. The feature at 1305 cm^{-1} corresponds to the vibrations of CH_2-chains with a considerable amount of *gauche* conformers, which are localized in the amorphous phase. For the PE/PP blends under study, the Raman band at 1305 cm^{-1} has low intensity. In case of the PE/PP blends we observed this band obviously only for the sample with the PE content of 13 wt. %. For other samples the feature at 1305 cm^{-1} appeared only as small asymmetry of the line at 1295 cm^{-1}.

Except for a doublet in the spectral region from 1424 to 1500 cm^{-1}, the Raman lines of the PE vibrations do not overlap with the Raman lines of the PP vibrations (Fig. 1). Homopolymers PE and PP are thermodynamically incompatible [5], therefore the Raman-active vibrations in the spectra of the PE/PP blends have the same symmetry as the corresponding vibrations in the spectra of neat PE and PP. Thus, in order to evaluate the conformational and phase composition of the PE/PP blends, we suggest applying the quantitative methods of analysis of supramolecular structure suggested by Strobl and Hagedorn for neat PE [8] and by Nielsen *et al.* for neat PP [7].

Namely, we calculated the characteristics of conformational and phase composition of the PE/PP blends from the Raman spectra using the following formulas, in analogy to the already established formulas for the same characteristics of homopolymers PE and PP [6,7].

$$\alpha_{cr-PP} = \frac{I_{809}}{I_{809}+I_{830}+I_{841}} \times 100\% \qquad (1)$$

$$\alpha_{trans} = \frac{I_{1295}}{I_{1295}+I_{1305}} \times 100\% \qquad (2)$$

$$\alpha_{cr-PE} = \frac{I_{1415}}{k(I_{1295}+I_{1305})} \times 100\% \qquad (3)$$

Here, α_{cr-PP} and α_{cr-PE} are contents of the orthorhombic PP crystallites and PE crystallites, respectively, α_{trans} is the total content of CH$_2$ chains in *trans*-conformation, i.e. the total content of the PE crystallites and the CH$_2$ *trans*-chains in the amorphous phase. The I_{809}, I_{830}, I_{841}, I_{1295}, I_{1305}, and I_{1415} are integral intensities of the Raman lines at 809, 830, 841, 1295, 1305, and 1415 cm^{-1}, respectively. The calibrating coefficient $k = 0.43$ was determined from Raman spectrum of solid *n*-alkane C$_{36}$H$_{72}$.

In our previous research [6], we used the formulas (2) and (3) to determine the content of PE crystallites (α_{cr-PE}) and the content of CH$_2$ chains in *trans*-conformation (α_{trans}) in the reactor PE/CEH blends. Fig. 3 shows these values for the nascent reactor PE/CEH blends under study. Fig. 4 shows the values of α_{cr-PP}, α_{cr-PE}, and α_{trans} for the PE/PP blends, which are calculated by using the formulas (1-3). Note, that we applied the formulas (1-3) without any normalization to the relative content of the blend components (PE and PP).

The value α_{cr-PE} for the source UHMW PE is equal to 72 %. We could not find the band at 1305 cm^{-1} neither visually analyzing the UHMW PE spectrum nor using the deconvolution procedure. For this reason we give the approximate value more than 72 % for α_{trans} for the neat UHMW PE sample. Comparing the values α_{cr-PE} and α_{trans} we found out, that the amorphous phase of the nascent reactor

PE/CEH blends consists of the CH$_2$-chains with numerous *gauche* -conformers, i.e. is fully disordered. Moreover, the amount of *gauche*-conformers increases dramatically with the increasing the growth of content of 1-hexene in the CEH or the amount of CEH in the PE/CEH blends (Fig. 3).
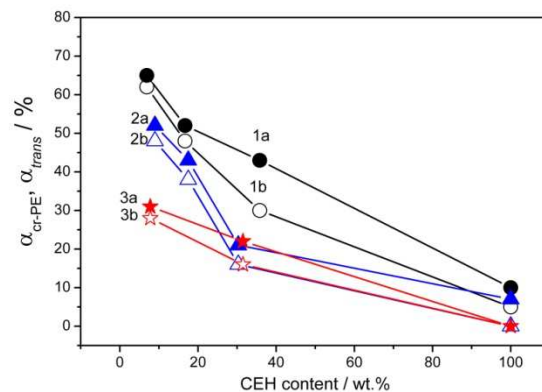

Fig. 3. The values α_{cr-PE} and α_{trans} *versus* the CEH content in the reactor PE/CEH blends: the curves 1a and1b correspond to 10.9 mole % of 1-hexene in the CEH, the curves 2a and 2b correspond to 19.9 mole % of 1-hexene in the CEH, the curves 3a and 3b correspond to 37.0 mole % of 1-hexene in the CEH. The symbols "a" and "b" mark α_{trans} and α_{cr-PE}, respectively.
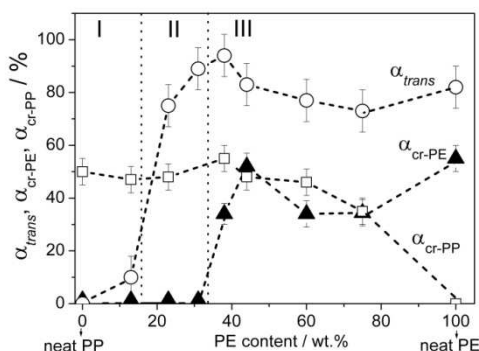

Fig. 4. The values α_{trans}, α_{cr-PE}, and α_{cr-PP}, *versus* the PE content in the melt-mixed PE/PP blends.

We found out, that the content of PP crystallites (α_{cr-PP}) in the PE/PP blends depends weakly on the PE content. For all the PE/PP blends under study, except for the blend with the PE content of 75 wt.%, the values of α_{cr-PP} were equal to about 50 % that is close to the degree of crystallinity of the neat PP. Considerable decrease in the content of PP crystallites was observed only for the blend with the PE content of 75 wt. %, for which the value α_{cr-PP} was equal to about 35 % (Fig. 4). The PE conformational and phase compositions depend strongly and non-monotonously on the PE content in the PE/PP blends. According to the changes of these structural characteristics we graded all the samples into three groups. The Group I includes the samples with low PE content in the blends: 0 (neat PP) and 13 wt. %. At the PE content of 13 wt. % in the blend, the PE molecules contain the numerous *gauche*–conformers (about 90%), and,

correspondingly, a few *trans*-conformers (about 10%). The orthorhombic PE crystallites are absent. Thus, the PE molecules form only disordered amorphous phase at PE content of 13 wt.% in the PE/PP blend. With increasing the PE content in the PE/PP blends until 38 wt. %, an amount of *trans*–conformers increases, i.e. CH_2-chains form ordered amorphous phase (Fig. 4). However, the Raman spectra still point to the absence of the orthorhombic PE crystallites in the PE/PP blends. The orthorhombic PE crystallites appear only at the PE content ≥ 38 wt. %. Therefore, we include in the Group II the samples with middle PE content in the blends: 23 and 31 wt.%. In these samples the CH_2-chains form well–ordered amorphous phase with the considerable amount of *trans*-segments. The Group III includes the samples with high PE content in the PE/PP blends: 38, 44, 60, and 75 wt. %, as well as the neat PE. According to the Raman spectra and calculations by using the formulas (2) and (3), the PE macromolecules form both the orthorhombic PE crystallites and the amorphous phase in these samples. In turn, the PE macromolecules in the amorphous phase contain both *trans*-conformers about 30-40 % and *gauche*- conformers about 20-30%.

We think, that a reason of the non-monotonous changes in the conformational and phase compositions of PE in the melt-mixed PE/PP blends are different conditions for forming the PE phases in the blends due to different melting temperatures of PE (118 ^{o}C) and PP (176 ^{o}C). In particular, at low PE content the PE/PP blends can be considered as composite of PP with the amorphous filler PE. Opposite, at high PE content, the PE/PP blends can be considered as composite of PE with semicrystalline filler PP.

Conclusions

We concluded that Raman spectroscopy can be effectively applied for nondestructive quantitative analysis of the conformational and phase compositions of PE-based blends.

We carried out detailed Raman structural study of melt-mixed blends of linear low-density polyethylene (PE) and isotactic polypropylene (PP). The relative content of PE in the PE/PP blends varied from 13 to 75 wt. %. Also we studied a structure of the amorphous phase of the reactor blends of PE and random ethylene/1-hexene copolymer (CEH). We found out, that the CH_2 chains in the amorphous phase of the PE/CEH blends contain the numerous *gauche*- conformers at any content of the CEH in the blend or 1-hexene in the CEH.

We showed, that for the PE/PP blends a relative content of the PE orthorhombic crystalline phase, a total amount of *trans*-conformers in CH_2-chains,

and a relative content of the crystalline phase of isotactic PP can be quantified by using the equations suggested by Strobl and Hagedorn for neat PE and by Nielsen *et al.* for neat PP.

Our Raman spectroscopic study revealed that the content of the crystalline phase of isotactic PP depends weakly on the relative content of blend components (PE and PP). Except for the blends with high PE content (more than 60 wt. %), the PP crystallinity in the blends coincides approximately with the crystallinity of the source PP. Opposite, owing to different melting temperatures of PE (118 ^{o}C) and PP (176 ^{o}C) the PE phase and conformational compositions in the melt-mixed PE/PP blends depend significantly on the PE content. The PE macromolecules form only an amorphous phase with different proportions of *trans*-/*gauche*- conformers at low and middle PE contents (< 38 wt. %). At high PE content (38% and higher) the PE macromolecules form both the orthorhombic crystalline phase and the amorphous phase with different proportions of *trans*-/*gauche*-conformers.

Comparing structure of the amorphous phases in the melt-mixed PE/PP blends and the nascent reactor PE/CEH blends, we concluded, that the conformational composition of CH_2-chains in the amorphous phase depends on the chemical structure of the second component in PE-based blends.

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