acta physica slovaca vol. 55 No. 6, 577 – 587 December 2005

MECHANICAL AND NUCLEAR MAGNETIC RESONANCE STUDY OF LOW DENSITY POLYETHYLENE, POLYPROPYLENE AND THEIR BLENDS

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Received 19 July 2005, in final form 27 October 2005, accepted 28 October 2005

Low-density polyethylene (LDPE) and isotactic polypropylene (PP) and their blends with compositions 90/10, 70/30, 50/50, 30/70 and 10/90 weight per cent were studied by means of mechanical and nuclear magnetic resonance (NMR) methods. The three types of tapes were prepared: undrawn, drawn up to complete neck development and ultimately drawn up to break. The macroscopic properties characterized by tensile modulus, ultimate strength and drawability as well as phase structure and macromolecular orientation were studied by these methods. It was found out that properties of studied materials vary with composition and with degree of drawing. Quantitative relations were found out between macroscopic properties obtained from mechanical measurement and parameters characterizing phase structure and macromolecular orientation obtained from NMR measurements.

PACS: 61.41.Pe, 82.35.Lr, 62.20.Fe, 81.40.Lm

1 Introduction

Blending and chemical and physical modifications of “bulk commodity polymers” (such as polyethylene, polypropylene, polyvinylchloride, polystyrene) are intensively used in polymer research and industry. By means of these modifications the properties of new multicomponent polymeric materials may be improved with respect to their components alone [1,2]. These properties may be further influenced by mechanical and/or thermal treatment. Between variety of blends made of two or more polymers those consisting of polyethylene (PE) and polypropylene (PP) are subject of interest from scientific as well as practical point of view [3].

In this paper we are dealing with the study of materials based on low-density polyethylene (LDPE) and isotactic polypropylene (PP). Blends of these polymers (denoted as PE/PP) with different composition have been prepared and studied by means of mechanical and nuclear magnetic resonance (NMR) methods.

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This paper follows our previous studies devoted to PE/PP blends (undrawn and drawn) with $70/30$ and $50/50$ compositions [4–6]. It was found out that LDPE and PP are immiscible, drawn and undrawn samples have different glass-transition temperatures T_g and that deformation of PE and PP differs each other. For the present work slabs of isotropic (undrawn) denoted as the C–type and two kinds of oriented tapes denoted as the B–type drawn up to complete necking and the A–type ultimately drawn up to break were used. Mechanical testing of the materials provides such quantities as Young modulus (E), ultimate strain (ε_u) and ultimate stress (σ_u). Wide-line NMR spectra provide a set of parameters characterizing the phase structure and macromolecular mobility in the studied samples. For drawn samples (A, B) the NMR spectra were measured also as a function of the angle between draw–direction and the external magnetic fieled induction. Parameters C_4, C_2 and C_0 characterizing the anisotropy of the second moment of the NMR spectra were derived from experimental data. Some preliminary results concerning the anisotropy of the NMR second moments for ultimately drawn samples were published in our paper [7]. Evaluation of mechanical and NMR measurements were carried out at ambient temperature.

2 Experimental

2.1 Materials and Methods

The following commercially available polymers were used in this work: LDPE (Bralen RA–2–63) with melt flow index (MFI) $2.0\mathrm{g}/10\mathrm{min}$, density $\rho = 915\,\mathrm{kg\,m^{-3}}$, softening temperature $T_\mathrm{m} = 92\,°\mathrm{C}$; isotactic polypropylene (PP) with $\mathrm{MFI} = 10\mathrm{g}/10\mathrm{min}$, $\rho = 903\,\mathrm{kg\,m^{-3}}$ and $T_\mathrm{m} = 153\,°\mathrm{C}$. Samples with different concentrations of components LDPE and PP, characterized by weight fraction of PP ($\mathrm{x_{PP}}$) with $\mathrm{x_{PP}} = 0, 0.1, 0.3, 0.5, 0.7, 0.9$ and 1.0 were prepared in a Brabender plasticorder PLE 331 at temperature of 190 °C for 27 min with the mixing rate of 35 rpm. Samples were compression moulded at 190 °C for 1 minute. Three kinds of samples in the form of slabs were prepared from homopolymers (PP and LDPE) as well as from their blends: undrawn (denoted as C–type), drawn to complete neck formation (B–type) and ultimately drawn up to their failure (A–type). The tensile properties were measured at room temperature (22 ± 1 °C) on the dog-bone specimens using an Instron testing machine at the crosshead speed of $10\,\mathrm{mm/min}$. The broad–line ^{1}H NMR measurements were performed with the continuous wave spectrometer which operates at the fixed magnetic field $B_0 = 0.247\,\mathrm{T}$ using frequency sweep through resonance region [8]. For the NMR line–shape analysis NMR spectra were measured at three stabilized temperatures: -130 °C, -70 °C and $+22$ °C. Measurements were carried out on specimens in the form of strips (approximately 1 mm thick, 5 mm wide and 20 mm length), which were cut from undrawn and drawn samples. For line shape analysis the rectangular strips of drawn samples were stacked in a glass–tube with the draw direction parallel to the tube axis and perpendicular to the external magnetic field $\boldsymbol{B}$. The anisotropy of NMR spectra and their second moments was measured for drawn samples (B– and A–type) at room temperature in such a way that it was possible to change the angle ϑ between draw direction and magnetic field $\boldsymbol{B}$ by means of a protractor connected with a sample holder with the accuracy of $\approx \pm 2°$. The values of ϑ were changed by $10°$ steps from $-10°$ up to $+100°$; we put $\vartheta = 0°$ when draw direction was parallel to $\boldsymbol{B}$. The second moments (M_2) of NMR spectra were calculated by means of numerical integration of measured spectral function $F'(x)$ in derivative form $F'(x) = \mathrm{d}F(x)/\mathrm{d}x$ according to relation [9]

$$M_2 = \frac{1}{3}\frac{\int x^3 F'(x)\mathrm{d}x}{\int xF'(x)\mathrm{d}x}, \tag{1}$$

where $x = B - B_0$ is a deflection of the external magnetic field B related to the resonance value B_0. The second moments were determined with the accuracy better than $\pm 0.5 \times 10^{-8}\,\mathrm{T}^2$.

2.2 Mathematical treatment of experiments

The broad-line NMR spectrum of partially crystalline polymer measured at temperatures sufficiently above it's glass transition temperature T_g usually consists of three elementary spectra: y_n (narrow), y_m (middle) and y_b (broad). The y_n component is related to non-crystalline – amorphous regions with micro-Brownian motion of chains and the medium component y_m corresponds to the regions with hindered motion of chains in the intermediate regions between the crystalline and amorphous regions. The broad component y_b arises from resonanting nuclei (^{1}H in our case) situated in crystalline regions as well as from others parts of the material with highly restricted motions of chains [10–13]. In our case all NMR spectra measured at room temperature were analysed according to the modified Bergmann's method [13]. The narrow and middle spectral functions we took in the form of product of the Gaussian and Lorentzian functions [10, 12] and the broad elementary spectrum y_b was derived from the NMR spectrum measured at temperature $T < T_g$ (-130 °C in our case). The spectrum y_c calculated in terms of elementary spectra y_i (i stands for n, m, b) was expressed by the equation

$$y_c(x) = w_n y_n(x, \beta_n^L, \beta_n^G, B_{\mathrm{mod}}) + w_m y_m(x, \beta_m^L, \beta_m^G) + w_b y_b(x, s), \tag{2}$$

where $x = B - B_0$, w_n, w_m and w_b are the respective weight factors which represent the relative number of resonanting nuclei belonging to the corresponding regions represented by elementary spectral functions y_i. The parameters $\beta_\alpha^L, \beta_\alpha^G$ ($\alpha = n, m$) and s determine the widths of the elementary spectra. The influence of the modulation field B_{mod} on the narrow elementary spectrum was considered according to our paper [13]. All elementary spectra $y_i(x)$ as well as the whole spectral function $y_c(x)$ are normalized to unity, so the following relation holds: $w_n + w_m + w_b = 1$. Measured NMR spectra (at 22 °C) were analysed according to theoretical one, given by eq. (2) and the parameters $w_i, \beta_\alpha^L, \beta_\alpha^G$ ($\alpha = n, m$) and s were obtained by the least square method [13]. The difference between the experimental spectral function $F(x)$ in eq. (1) and the theoretical ones, $y_i(x)$, in eq. (2) is that the former is unnormalized. The denominator in eq. (1) ensures this normalization.

In uniaxially drawn polymer tapes (films and fibres as well) the macromolecular chains tend to align along the draw direction. Such situation would be expected for our samples of the B and A–type. The second moment of the NMR spectrum for oriented polymer may be anisotropic when recorded as a function of the sample orientation in the magnetic field of the NMR spectrometer. For uniaxially oriented sample with isotropic transversal distribution of macromolecular chains the expression for NMR second moment M_2 may be written in the form [9, 14–17]

$$M_2 = C_4 \cos^4\vartheta + C_2 \cos^2\vartheta + C_0, \tag{3}$$

where ϑ is the angle between draw direction and magnetic field $\boldsymbol{B}$. Parameters C_i depend on spacial configurations of resonanting nuclei in the polymer chains, on their orientation and mobility [9, 15, 17].

The second moments were calculated for each spectrum recorded at a position of the sample characterized by the angle ϑ according to relation (1). Experimentally obtained dependences $M_2(\vartheta)$ were analysed according to eq. (3) and the parameters C_i $(i = 0, 2, 4)$ were determined by means of the least square procedure. As it may be seen from eq. (3) the anisotropy of the second moment is characterized by the two parameters C_4 and C_2, which are zero for unoriented (isotropic) sample and they reach maximal values C_{4m}, C_{2m} for ideally–complete orientation of all chains in one direction. The parameters C_4 and C_2 may be thought as a measure of an overall (mean) macromolecular orientation because in eq. (3) different orientation states in crystalline and noncrystalline regions were not taken into account.

3 Results and discussion

3.1 Homopolymers LDPE and PP

The results of our experiments performed on homopolymers LDPE and PP and on blends of these components are visualized in Figs. 1–6 and in Tab. 1. As it may be seen from these data the properties of LDPE and PP measured at room temperature differ significantly: Young modulus (E), strength (σ_u) and drawability (ε_u) are greater for PP when compared with LDPE (see Fig. 1). The phase structure of LDPE is represented by three spectral functions y_i $(i = n, m, b)$ with the weight factors $w_n^C = 0.1$ and $w_m^C = w_b^C = 0.45$ for undrawn sample (Fig. 2, 4). The weight factor $w_b^C = 0.45$ coincides well with the crystallinity $x_c = 0.47$ calculated from measured density $\rho = 915\,\mathrm{kg/m^3}$, with crystalline $\rho_c = 1000\,\mathrm{kg/m^3}$ and amorphous $\rho_a = 850\,\mathrm{kg/m^3}$ densities by means of relation $x_c = \frac{\rho-\rho_a}{\rho_c-\rho_a}\frac{\rho_c}{\rho}$ [2, 18].

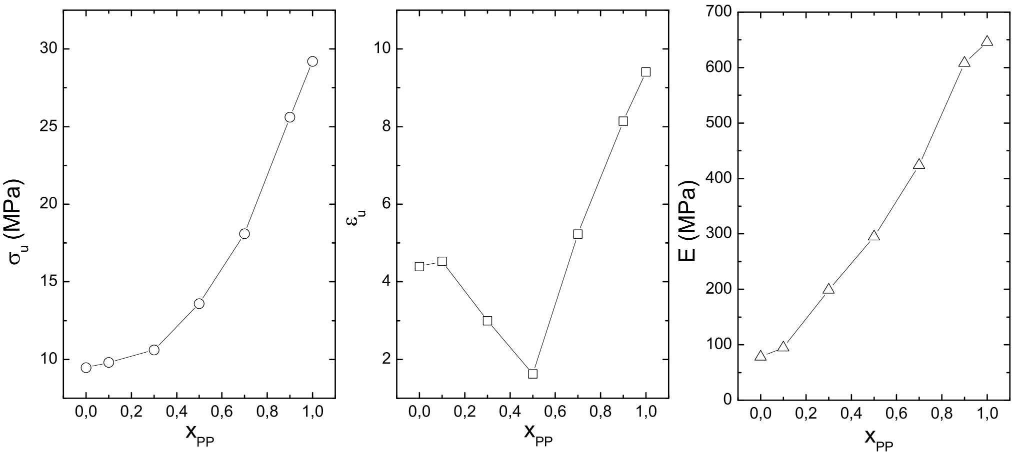

Fig. 1. Dependences of ultimate strength (σ_u), relative elongation at break ($\varepsilon_u = l_\mathrm{b}/l_0$) and tensile modulus ($E$) on concentration $\mathrm{x_{PP}}$.

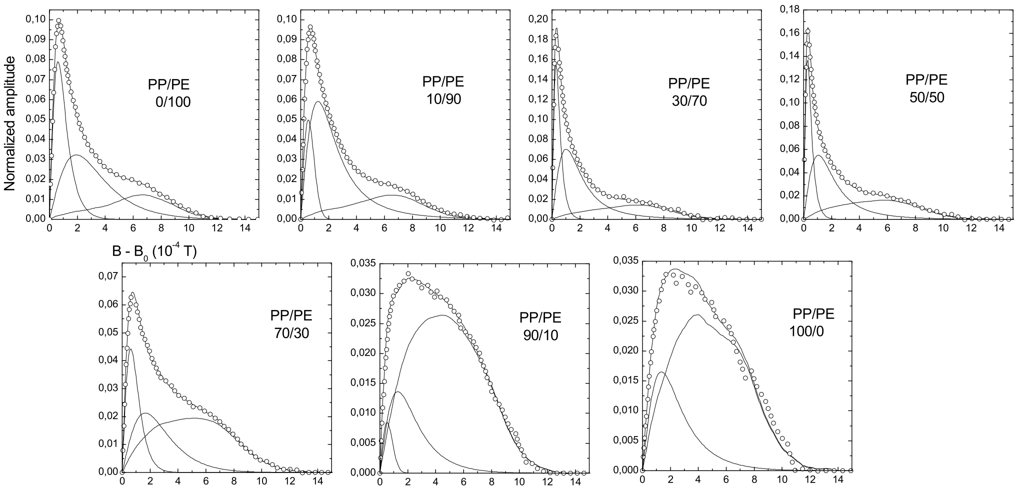

Fig. 2. Halves of the normalized NMR spectra in derivative form for undrawn (C–type) LDPE, PP and their blends. Selected experimental points of NMR spectra together with calculated elementary spectra y_n, y_m, y_b and a total spectral function y_c are shown (solid lines).

The glass–transition temperatures T_g, derived from our former NMR measurements [6], were near $-73\,^\circ$C for undrawn and $-23\,^\circ$C for highly drawn LDPE, respectively. As we may see the room temperature ($T_r = 22\,^\circ$C) is sufficiently higher than T_g's for different kinds of LDPE (A–, B– and C–type, respectively). The phase structure remains practically unchanged for sample drawn up to complete necking (B–type) and the weight factors are: $w_n^B = 0.09, w_m^B = 0.44$ and $w_b^B = 0.46$. For ultimately drawn sample (A–type) the changes in weight factors are not so significant as it would be expected, they are: $w_n^A = 0.04, w_m^A = 0.43$ and $w_b^A = 0.53$. The widths of spectral components are: for narrow $\delta_n^C = 1.05 \times 10^{-4}$T, $\delta_n^B = \delta_n^A = 1.3 \times 10^{-4}$T; for middle $\delta_m^C = 3.8 \times 10^{-4}$T, $\delta_m^B = 4.0 \times 10^{-4}$T, $\delta_m^A = 3.9 \times 10^{-4}$T – they are practically equal $\delta_m = 3.9 \times 10^{-4}$T; and for broad $\delta_b^C = 13.5 \times 10^{-4}$T, $\delta_b^B = 15.5 \times 10^{-4}$T, $\delta_b^A = 14.0 \times 10^{-4}$T.

Despite of the relative small changes in the phase structure (w_i) and in the widths of the spectral functions (δ_i) there are greater changes in macromolecular orientation caused by drawing. As we may see from Fig. 3 and Tab. 1 the angular dependences for NMR second moments $M_2(\vartheta)$ and parameters C_i are clearly different for samples B and A, respectively. These data suggest that the orientation of macromolecules in LDPE increases progressively from isotropic (unoriented) state through necking up to the failure of the material.

Concerning polypropylene (PP), the weight factors w_i are significantly different from those for LDPE. There is a negligible amount of narrow ($w_n = 0 \div 0.004$) and a small amount of middle component ($w_m = 0.06 \div 0.13$). Broad component is dominant in the NMR spectra for all three types of PP samples: $w_b = 0.86 \div 0.87$ (for C– and B–type) and $w_b = 0.93$ for A– type. Crystallinity $x_c = 0.59$, calculated from measured density with $\rho_c = 950\,\mathrm{kg/m^3}$ and $\rho_a = 850\,\mathrm{kg/m^3}$ [2] is very different from values of w_b stated above. It suggests that the NMR spectra measured at room temperature (22 °C) do not reflect the real phase structure because this temperature is not sufficiently above T_g's for PP which are $-13\,^\circ$C for undrawn and $+17\,^\circ$C for highly drawn PP, respectively [6]. These data show that the mobility of macromolecular chains in the noncrystalline regions is still very low at room temperature. A macroscopic manifestation of this motional state is higher value of modulus E and strength σ_u for PP when compared with LDPE where mobile components y_n and y_m are already clearly manifested. The widths of broad components are for all three types of PP nearly equal $\delta_b \approx 8.0\times10^{-4}$T ($\delta_b^C = 8.0\times10^{-4}$T, $\delta_b^B = 8.2\times10^{-4}$T, $\delta_b^A = 7.9\times10^{-4}$T). The middle components have the widths $\delta_m^C = 2.7\times10^{-4}$T, $\delta_m^B = 4.4\times10^{-4}$T, $\delta_m^A = 4.2\times10^{-4}$T, respectively. The significant difference in the widths of the broad component for LDPE ($\delta_b \approx 14\times10^{-4}$T) and PP ($\delta_b \approx 8\times10^{-4}$T) is caused by different chemical composition of monomer units. In polypropylene the methyl groups (CH_3) perform fast rotation about C_3 axis of symmetry already at temperatures lower than -200 °C [17, 19]. This motion is equally effective in crystalline as well as in noncrystalline regions.

The analysis of the angular dependences (Fig. 3 and Tab. 1) shows that the respective parameters C_4 and C_2 differ only a little for B– and A–type samples, but they are somewhat greater for A–type in respect to those for B–type. It suggests that drawing of PP tapes after complete necking up to their failure does not change appreciably the degree of macromolecular orientation. Hence the orientation processes caused by drawing in LDPE and PP are realized by different ways.

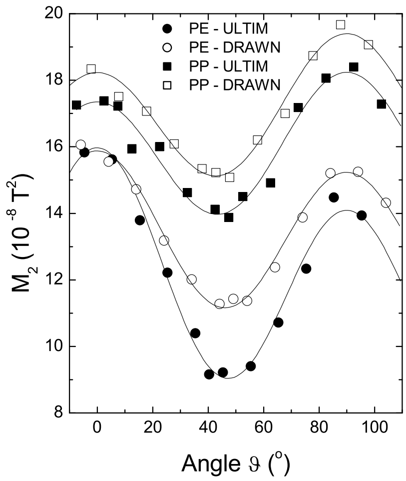

Fig. 3. The dependences $M_2(\vartheta)$ for drawn LDPE and PP tapes; ULTIM means drawn up to break (A–type), DRAWN means drawn up to complete necking (B–type). Solid lines drawn through experimental points are fit according to eq. (3).

3.2 Blends of LDPE and PP

Now we shall discuss results concerning the PE/PP blends. Our analysis is based on the dependences of measured quantities with respect to composition, characterized by weight fraction of PP, denoted as x_{PP}.

As we can see from Fig. 1 all three quantities (E, σ_u and ε_u) characterizing the mechanical properties in a full composition range show negative differences from the additive rule between the pure blend components. The most significant differences are manifested in elongation at

	B–type (non broken)			A–type (broken)		
$\mathrm{X_{PP}}$	C_4	$-C_2$	C_0	C_4	$-C_2$	C_0
1.0 (PP)	14.67	15.84	19.40	15.24	16.13	18.24
0.9	16.13	15.90	17.33	17.26	17.18	17.51
0.7	18.61	18.57	17.47	19.47	19.30	16.12
0.5	–	–	–	20.49	19.41	15.33
0.3	20.12	19.21	15.52	20.73	19.52	14.61
0.1	21.80	21.32	15.81	24.11	21.59	14.23
0.0 (LDPE)	17.55	16.91	15.23	23.82	21.94	14.09

Tab. 1. Parameters C_4, C_2 and C_0 (expressed in $10^{-8}\mathrm{T}^2$) characterizing dependences of $M_2(\vartheta)$ for drawn samples of A– and B–types.

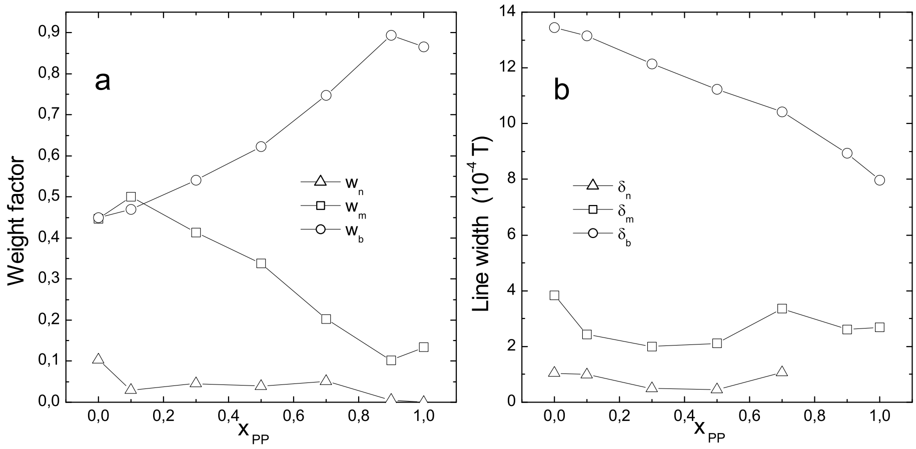

Fig. 4. (a) Weight factors w_n, w_m and w_b and (b) widths of elementary spectra δ_n, δ_m and δ_b in respect to the composition x_{PP} for undrawn (C–type) samples of LDPE, PP and PE/PP blends.

break, ε_u, which characterizes drawability of the material. Drawability of LDPE does not change appreciably by addition of PP up to $\mathrm{x_{PP}} = 0.1$ (i.e. $10\,\%$ PP). At higher concentrations of PP it decreases and at $\mathrm{x_{PP}} \approx 0.5$ drawability reaches minimum. For this reason it was impossible to prepare tapes of B–type with this composition because they broke already at low elongation without necking. This behavior is typical for incompatible blends with poor stress transfer between the phases through the phase boundaries. Because of week interface (usually due to low adhesion and negligible intermixing of molecules on the phase boundaries), the catastrophic crack is formed at low deformation and the material manifests itself as brittle. This behavior is observable mainly for elongation at break dependences on composition; Young's modulus values of composites multiphase systems usually follow the rising trend with addition of stiffer component regardless the quality of adhesion between the phases. The tensile strenght is rather complex parameter, depending on both modulus and elongation value and even for incompatible systems its dependence on the composition does not necessarily reaches any minimum. The negative deviation from the additivity rule is almost always observed, similar as for our blends as seen in

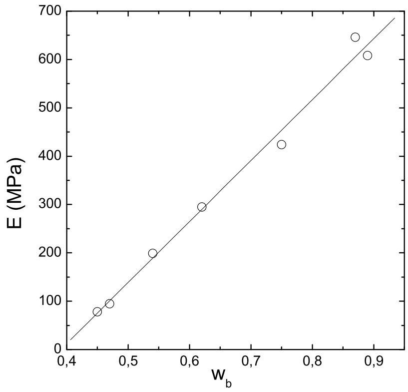

Fig. 5. The dependence of tensile modulus E on the weight factor of the broad component w_b for undrawn samples (C–type).

Fig. 1.

We have to mention that the structure, macromolecular orientation and mobility change during drawing, which starts from undeformed state through elastic deformation, followed by plastic deformation up to break of the material. Our NMR experiments represent the three states: undeformed (C), final stage of plastic deformation–complete necking (B) during which plastic flow of macromolecules occurs without extensive deformation of the macromolecular chains and the state of ultimate deformation–failure (A) where the main molecular reason for deformation is stretching and significant orientation of macromolecules resulting in a formation of fibrillar structure and usually accompanied by orientation crystallization.

We shall start from analysis of the NMR spectra for undrawn tapes (C–type), which are displayed in Fig. 2 together with the elementary spectra y_i $(i = n, m, b)$. The weight factors w_i and the widths δ_i are shown in Fig. 4a, b as a function of composition $\mathrm{x_{PP}}$. As it is here demonstrated the narrow spectral lines appear only in samples containing LDPE up to concentration $\mathrm{x_{PP}} \approx 0.7$. At lower amounts of LDPE the narrow component is negligible, with $w_n \leq 0.01$. It suggests that the narrow lines may be ascribed to the mobile chains of LDPE. The narrow component is not observed in neat PP. The widths of narrow lines vary between $\delta_n = 0.5 \times 10^{-4}$T (for $\mathrm{x_{PP}} = 0.3$ and 0.5) and $\delta_n = 1.1 \times 10^{-4}$T (for $\mathrm{x_{PP}} = 0, 0.1$ and 0.7), respectively. The greatest amount of amorphous fraction belongs to neat LDPE where $w_n = 0.1$. Addition of PP to LDPE lowers this fraction to the value of $w_n = 0.05$, which is constant up to $\mathrm{x_{PP}} = 0.7$ and then practically vanishes.

The middle component y_m representing noncrystalline chains with restricted motions is present in NMR spectra of all samples. Their weight factors w_m are above the additivity line for concentrations $\mathrm{x_{PP}}$ between 0.0–0.7, on the expense of the decrease of weight factors of narrow $(\Delta w_n \approx 0.05)$ and broad component, respectively. For sample with $\mathrm{x_{PP}} = 0.9$ (without measurable y_n) the weight factor w_m is below and w_b is above the corresponding values followed from additivity rule. The widths δ_m are nearly equal $(\delta_m \approx 3 \div 4 \times 10^{-4}$T) for samples with $\mathrm{x_{PP}} = 0, 0.7, 0.9$ and 1.0, but for lower concentrations $\mathrm{x_{PP}} \approx 0.1 \div 0.5$ the narrowing of y_m component with $\delta_m \approx 2.0 \times 10^{-4}$T is observed. This together with the coarse of weight fractions w_m and widths δ_n suggests that some amorphisation occurs in blends with $\mathrm{x_{PP}}$ ranging from 0.1

to 0.5.

A higher amount of intermediate phase and narrowing of the corresponding spectral component (y_m) may be caused by restrictions for crystallization of LDPE, imposed by the presence of solid PP particles due to considerable different softening temperatures of homopolymers, which are $92\,°\mathrm{C}$ for LDPE and $153\,°\mathrm{C}$ for PP, respectively.

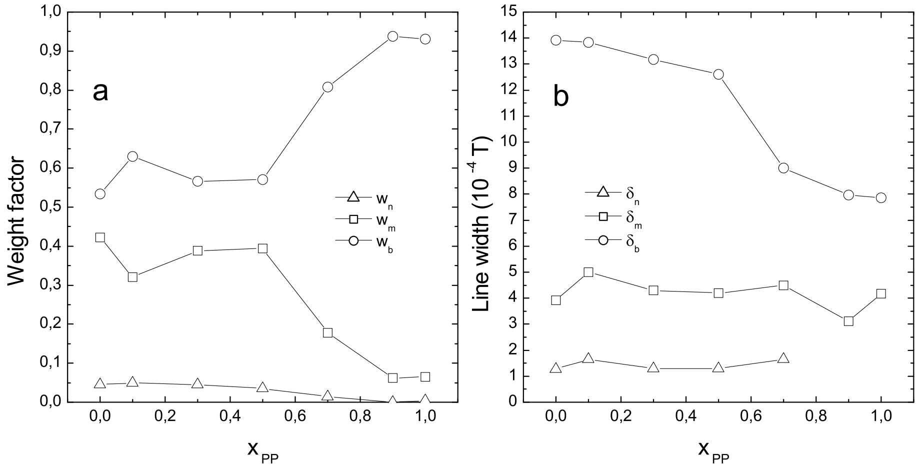

Fig. 6. (a) Weight factors w_n, w_m and w_b and (b) widths of elementary spectra δ_n, δ_m and δ_b in respect to the composition $\mathrm{x_{PP}}$ for ultimately drawn (A–type) samples.

Despite of the overall increase of the "immobile" fraction, represented by the spectral function y_b, values of w_b are below additivity line for $\mathrm{x_{PP}} \leq 0.7$. As it was mentioned previously, broad component represents not only crystalline regions of the material. The elastic properties of samples would be determined by all structural units with highly restricted motion. Hence, a correlation between tensile modulus E and weight factor w_b would be expected. This is demonstrated in Fig. 5 for undrawn PE/PP blends, where linear dependence is evident. The width δ_b of the broad spectral component decreases with $\mathrm{x_{PP}}$. Besides of the weight factors w_b, this parameter depends on the shapes of $y_b(x, s)$, on their widths and on scaling parameters s for individual components LDPE and PP, respectively. The scaling factor s varies between 0.90 and 0.95 with the mean value of 0.91 ± 0.01, which indicates a small narrowing of the broad components for both homopolymers at room temperature in respect to those, measured at the lowest temperature ($-130\,°\mathrm{C}$).

Now we shall deal with drawn samples, first with the ultimately drawn ones (A–type). NMR measurements have been performed on samples cut from undamaged parts of the broken tapes. Macroscopic fibrils are seen on the edges of these tapes, suggesting that significant changes in the structure of the materials were realized at the final stages of deformation. NMR spectra of drawn samples have the form similar to those for undrawn ones, but with different values of parameters w_i, δ_i and s. The results of their analysis for ultimately drawn tapes (A–type) are presented in Fig. 6a, b. Because the behaviour of the spectral parameters (w_i, δ_i, s) with respect to composition ($\mathrm{x_{PP}}$) for samples of B–type is "between" those for C– and A–type, we shall not present them in this article. As it may be seen from Fig. 4 and 6, the changes in the phase structure caused by deformation of these tapes depend on the polymer matrix formed by blending. For $x_{PP} \leq 0.5$ the LDPE matrix dominates. In this case the amount of narrow component w_n remains practically unaffected by deformation and is $w_n^C \approx w_n^B \approx w_n^A \approx 0.04$. A broadening of the narrow component is evoked by drawing with $\delta_n^B \approx \delta_n^A \approx 2\delta_n^C$.

The mass fraction of the middle component w_m moderately decreases with the increasing deformation, i.e. $w_m^C > w_m^B > w_m^A$. The broadening of this component is also observed and $\delta_n^B \approx \delta_n^A \approx 2\delta_n^C$. Such an increase in the line-widths of narrow and middle components indicates that the molecular chains in the noncrystalline regions which are mobile in original (undrawn) tapes, are more constrained by deformation with a resultant decrease in molecular chain mobility.

The fraction of the broad component increases with drawing so that $w_b^C \leq w_b^B < w_b^A$ on the expense of the middle component. The width δ_b increases with deformation up to complete necking and then decreases, so that inequality $\delta_b^C < \delta_b^A < \delta_b^B$ holds. It suggests that post-necking drawing resulted in the increase of amount of crystalline phase ($w_b \approx x_C$ for PE matrix), but with the structure different from that for the former states (C– and B–types). Narrowing of the broad component may indicate that the regions contained "immobile" chains, but loosely packed, are created at ultimate drawing.

For higher concentrations $x_{PP} > 0.5$ (where the continuous phase is PP) the amount of narrow component is negligible. A modest increase of w_m^B relative to undrawn state w_m^C but significant decrease of $w_m^A \approx 0.5 w_m^C$ is registered for ultimately drawn samples. For widths of the middle component the relations $\delta_m^C < \delta_m^A \approx \delta_m^B$ holds. The broad component dominates in the NMR spectrum in this concentration range with the small changes of weight factor w_b at the first stages of deformation ($w_b^B \approx w_b^C$) but with perceivable increase in the final state, where $w_b^A > w_b^C, w_b^B$. The width of the broad component with respect to the deformation behaves according to inequalities $\delta_b^B < \delta_b^A < \delta_b^C$, which indicates, that a slight narrowing of the broad component takes place by drawing, relative to original sample. These changes in the width of broad component differ from those in LDPE matrix. It indicates again that deformation processes in these two polymer matrices are different.

The anisotropy of the drawn tapes of PE/PP blends was studied by means of analysis of the NMR second moment according to eq. (3) and corresponding values of parameters C_4, C_2 and C_0 are listed in Tab. 1. Detailed analysis of these data shows that the dependences of parameters C_4 and C_2 for ultimately drawn tapes (A–type) on concentration x_{PP} are linear, following the additivity rule in the whole concentration range, including homopolymers [7]. Similar linear dependences have been found for samples of B–type, but only in concentration range x_{PP} from 0.1 up to 1. Values of C_4 and C_2 for neat LDPE are far off the additivity line. It suggests that a small amount of PP, introduced into LDPE matrix ($\approx$ 10 wt %), may significantly influence orientational processes in such blend. It may be important to notice, that weight factors w_b, w_m and line width δ_m, show some pecularities for the same blend with $x_{PP} = 0.1$ (see Fig. 6). The third parameter C_0 does not follow the linear dependence on concentration. The values of C_0^A and C_0^B are lower than those followed from additivity rule. As we may see from Tab. 1, $C_0^A < C_0^B$ suggesting that the dependences $M_2(\vartheta)$ for samples of A–type are shifted to lower values, when compared with the ones for samples of B–type. This negative shift of $M_2^A(\vartheta)$ relative to $M_2^B(\vartheta)$ correlate well with the changes of parameters characterizing spectral components y_m and y_b which indicate some kinds of amorphisation in the blends after post-necking drawing. The amorphisation may be a consequence of crazes, cracks or voids, created during destruction process.

4 Conclusion

Several deformation mechanisms, based mainly on electron-microscopic and X–ray diffraction methods, have been proposed in the past to describe the morphological changes during drawing of polymeric materials, but Peterlin's model [21] is currently accepted with some modifications [22, 23]. According to these models it is generally accepted that drawing completely changes original (lamellar) structure into a highly aligned fiber structure. This study has indicated that wide line NMR, as a non-invasive experimental method, provides valuable information on structure, macromolecular orientation and mobility also in complex polymer systems such as polymer blends. The variations of NMR spectra in respect to composition and the two different stages of uniaxial drawing have been found in PE/PP blends.

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