Macromolecular Orientation in Drawn Polypropylene, Polyethylene and their Blend, Studied by NMR

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Summary: Drawn tapes made of polypropylene (PP), low density polyethylene (LDPE) and of their PP/LDPE blend (70/30 w/w) were studied by means of broad-line NMR (Nuclear Magnetic Resonance). The parameters characterizing the anisotropy of the NMR second moments were used for estimation of macromolecular orientation in drawn tapes. A model for this particular blend was proposed on the basis of NMR experiments. According to this model the LDPE component of the drawn blend is oriented in a such extent as similarly drawn homopolymer unlike the PP component which is oriented to a much lower degree after drawing of the blend.

Introduction

Many important polymeric materials are actually not homogenous, but rather heterogeneous in terms of their chemical and/or physical structure. This applies equally for semicrystalline polymers, polymer blends, block copolymers and polymers mixed with filler materials. The combination of components in polymer blend can result in additive values of properties or values which are either superior or inferior compared to properties of any component of the blend.

A plastic deformation of such heterogeneous systems influences, in many cases significantly, the properties of resulting material. Deformation imposes the changes on supramolecular and on macromolecular level of the structure. Molecular dynamics is also altered and it influences macroscopic properties of materials such as brittleness or impact strength, mechanical moduli, creep, solid-state extrudability, absorption of energy from alternating mechanical or electromagnetic fields, etc.

Concerning polymer blends, combination of common polymers such as polyethylene, polypropylene, polystyrene etc, have been mainly investigated[1-3].

The present paper describes some properties of isotropic and drawn tapes prepared from 70/30 (w/w) blend of PP and LDPE as investigated by a broad-line nuclear magnetic resonance (BL-MNR). The method is capable to provide some useful information on

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molecular and on supramolecular level of structure. To facilitate comparison of the blend properties with those of its components, tapes of the PP and LDPE homopolymers were produced and investigated using the same procedure and conditions.

In our study we begin from the fact, that the second moment, M_2, of the NMR spectra for unaxially drawn polymeric fibres, foils or tapes may be expressed in a simple form$^{1-3)}$

$$M_2 = A.\cos^4\vartheta + B.\cos^2\vartheta + C, \quad (1)$$

where ϑ is the angle between the drawing direction and external magnetic field induction **B**. The quantities A, B and C depend on spatial configuration of the resonating nuclei (^1H – nuclei in our case) in the polymer chains, on the orientation of chains in a macroscopic sample and on the mobility of chains. Generally, the evaluation of these quantities involves laborious calculation even if the configurations of atoms in the polymer chains are known. Much more complicated situation arises when molecular motions have to be taken into account$^{4-6)}$. In spite of the difficulties with the existence of several phases in the individual components of the polymeric blends and with ill-defined of their structures and chain dynamics, an useful information concerning an overall orientation could be obtained from experimentally measured anisotropy of the NMR second moment fitted according to equation (1). As a measure of the anisotropy of the second moment and also of the overall macromolecular orientation, the values of the parameters A and B, as well as parameter p, defined as:

$$p = [\, ½\,(M_2(0°) + M_2(90°)) - M_2(\vartheta_m)\,] \,/\, M_2(\vartheta_m), \quad (2)$$

may be taken. ϑ_m is the angle for which M_2 has minimum. This angle can be expressed by a following formula: $\vartheta_m = \arccos\,(-B/2A)^{1/2}$. The parameter p may be expressed by quantities A, B and C as follows:

$$p = [\, 2A(A+B) + B^2\,] \,/\, (4AC - B^2). \quad (3)$$

For isotropic (unoriented) material quantities A, B and p are equal to zero and for completely oriented one, they reach the maximum values, given by the positions of atoms in the fully extended macromolecules and by their chain mobility. For partially oriented polymers, the higher are the values of A, B and p, the larger is the degree of anisotropy and orientation.

Preparation of the Materials and Experimental Conditions

The commercial polymer grades used in this work have following characteristics:

Isotactic polypropylene PP-TF411 with melt flow index MFI = 2.1g / 10min (ASTM 1238) with density $\rho = 0.890 \times 10^3$ kg.m^{-3}; $T_m = 166\,^0C$ (DSC);

Low density polyethylene LDPE - Bralen RA2-19 with MFI= 2.0g / 10min (ASTM 1238) and $\rho = 0.919 \times 10^3$ kg.m^{-3}; $T_m = 112$ ^{0}C (DSC). Both polymers are the commercial products of Slovnaft Bratislava (Slovak Republic).

Blend of PP and LDPE with the composition: 70 wt% of PP and 30 wt% of LDPE was prepared by mixing the components in a Brabender Plasticorder at temperature of 180 ^{0}C with a mixing time of 10 min. Tapes have been prepared at temperature of 190 ^{0}C under pressure applied for 5 min. Drawing of the tapes has been performed by means of an Instron 4301 testing equipment at room temperature (20 – 22 ^{0}C) up to complete necking, with a draw ratio $\lambda \approx 4.5$ for all samples.

The strips with dimensions (approximately) 1mm thick, 5mm wide and 20mm in length were cut from drawn tapes of PP, LDPE and blended PP/LDPE for NMR measurements. These rectangular strips were stacked in a glass-tube. A protractor connected with a sample-holder indicated the angle ϑ between the drawing direction and external magnetic field induction **B** with a scatter below $\pm 2^0$. The values of the angle ϑ were changed by 5^0 steps, from -5^0 up to $+95^0$. At least two NMR spectra were recorded at each position of the sample, to obtain averaged spectra and a mean value of the second moment. NMR spectra in a derivative form were recorded by means of a BL-NMR spectrometer (RYa 2301) at H^1 resonance frequency of 14.1 MHz. Measurements were carried out at room temperature (20-22 ^{0}C). The modulation magnetic field with a frequency of 35 Hz had a peak-to-peak amplitude B_m of 0.5×10^{-4} T for samples containing LDPE and of 0.75×10^{-4} T for PP samples. A time constant of a lock-in amplifier was 1 sec. Sweep rate of the external magnetic field (dB/dt) was 10^{-5} T.s^{-1}. The second moment was calculated for each NMR spectrum by measuring the derivative absorption intensity $F'(x)$ at a small intervals (approximately 0.2 G = 2×10^{-5} T) from the center of resonance signal. Second moments were calculated by means of a numerical integration according to relation:

$$M_2 = \frac{\int F'(x).x^3 dx}{3\int F'(x).x dx} \tag{4}$$

where $x = B - B_0$ is a deflection of the external magnetic field induction B, related to the resonance value B_0 and $F'(x)$ represents the first derivative of the absorption intensity with respect to x. The symmetrical shape of the absorption NMR line F(x) was assumed (in accordance with experiments) in relation for M_2, given by above stated formula. Second moments were determined from experimental spectra with the accuracy better than $\pm 0.5 \times 10^{-8}$ T^2.

Results and Discussion

As we can see from Fig.1, NMR spectra from drawn tapes of PP, LDPE and PP/LDPE blend change their shape with respect to the angle ϑ. The dependencies of the second moment on angle ϑ are shown in Fig.2. The curves drawn through experimental points represent the best fitting of experimental data according to equation (1). The parameters A, B, C and p obtained are listed in Tab.1.

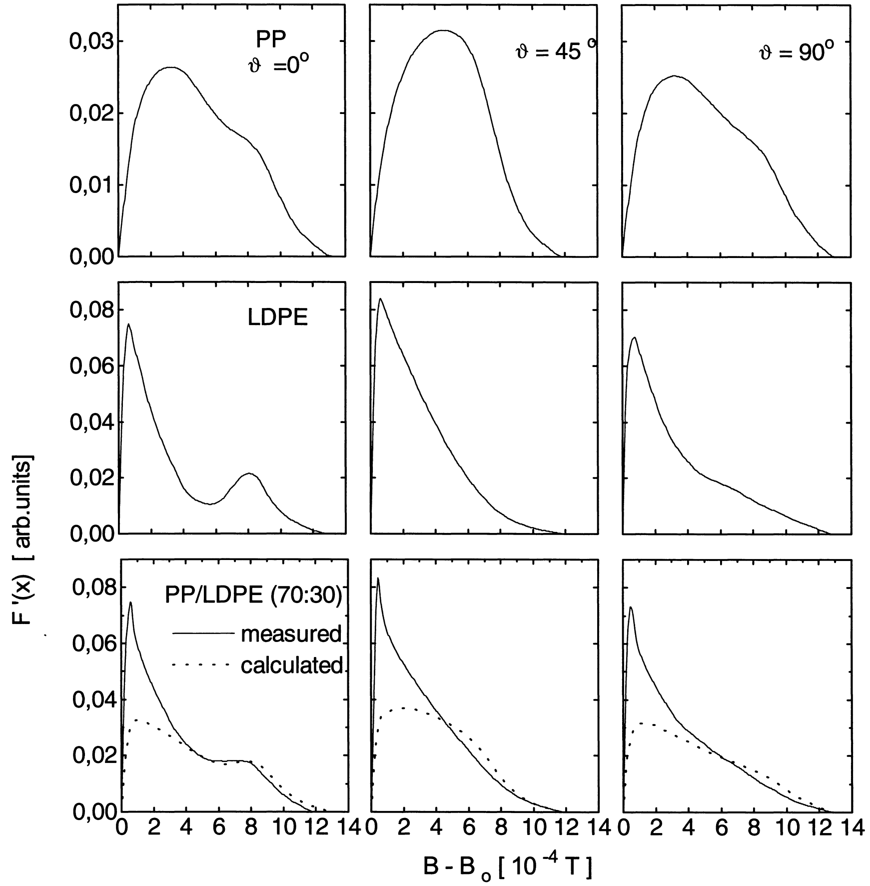

Fig.1. Halves of normalized NMR spectra for tapes of drawn PP, LDPE and PP/LDPE blend at three representative angles ϑ= 0^0, 45^0 and 90^0.

If the components of a polymer blend are assumed as immiscible, without any mutual interaction, then normalized NMR spectra and their second moments would be expressed as a weighted average of the component spectra and second moments.

The NMR spectra, $F'(x) = x_{PP}F'_{PP}(x) + (1 - x_{PP})F'_{PE}(x)$, calculated by means of the experimental spectra $F'_{PP}(x)$ and $F'_{PE}(x)$ for PP and LDPE, respectively, are shown in Fig.1 together with the experimental spectra for PP/LDPE blend (see the third row in the Fig. 1). The relative number of H^1 nuclei of the PP component is denoted as x_{PP} and it is identical with the weight fraction of this polymer in a particular blend ($x_{PP} = 0.7$ in our case). A significant difference can be seen between experimental and calculated spectra. This implies that addition rule does not hold for this blend and that changes in structure and / or molecular motion induced by drawing process are different from the drawing - induced changes in homopolymers.

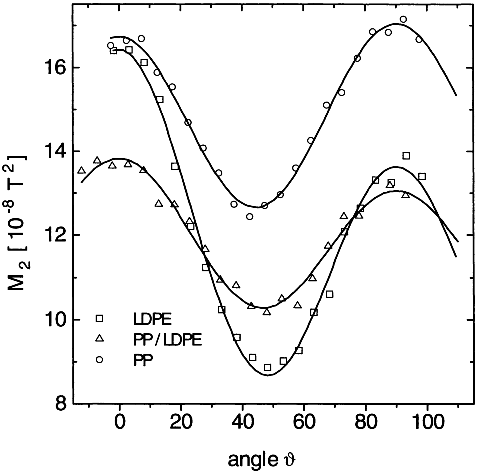

Fig.2. Angular variation of the second moment for drawn tapes with least-squares fit (solid lines) according to Eq.(1), measured at room temperature.

Two effects could be seen from measured and calculated NMR spectra :

(i) a narrow spectral component is observed for blend, representing highly mobile chains in amorphous (or disordered) regions of the material. This component is present also in LDPE component, but its contribution to compound spectra would be less pronounced than that observed in the blend.

(ii) a broad spectral component – anisotropic, representing crystalline and ordered regions, is narrower in spectra for PP/LDPE blend, than in the spectra for homopolymers.

As a measure of these differences quantity $\Delta M_{2\,i}$ is defined as :

$$\Delta M_2 = x_{PP}M_{2PP} + (1-x_{PP})\,M_{2PE} - M_{2BL}\,, \tag{5}$$

where symbols M_{2i} are corresponding second moments (i stands for PP; PE=LDPE; BL=PP/LDPE).

It is important to note at this place, that the differences ΔM_2 are close to zero for undrawn tapes of PP, LDPE and PP/LDPE blend in a broad temperature range[4)], suggesting a real immiscibility of the PP and LDPE components in an isotropic blend. However, nonzero and temperature dependent differences ΔM_2 have been obtained from temperature variations of the second moment for drawn blend[4)].

Table 1. Parameters determined from $M_2(\vartheta)$ dependencies

Tape	A 10^{-8} T^2	-B 10^{-8} T^2	C 10^{-8} T^2	p	ϑ_m
PP	16.87	17.18	17.03	0.333	44.5°
LDPE	25.09	22.30	13.63	0.733	48.2°
PP/LDPE	12.60	11.83	13.05	0.308	46.8°
Differences	ΔA	ΔB	ΔC		
	6.74	- 6.89	2.96	-	-

The anisotropy of the second moments for studied tapes may be estimated by means of the quantities listed in Tab.1. From Fig.2 we may conclude, that all drawn tapes are unaxially oriented because the angular dependencies agree well with relationship (1). The greatest anisotropy (measured by quantities A, B and p) was ascertained for LDPE and the least one for blend. The relationship for ΔM_2 applied on dependence $M_2(\vartheta)$ gives differences ΔA, ΔB and ΔC of the corresponding quantities A, B and C; so that $\Delta A = x_{PP}A_{PP} + (1 - x_{PP})\,A_{PE}$ and similarly for ΔB and ΔC, where A_i, B_i and C_i are derived from angular dependencies $M_2(\vartheta)$ for individual samples. As is see from Tab.1, magnitudes of these differences are much larger than zero. From this result we can infer that the PP and LDPE components have different responses to deformation process in a blend in comparison to responses of homopolymers deformed by a similar way. The differences ΔM_2 in the values of second moment, as well as, differences ΔA, ΔB and ΔC may be diminished, if they are calculated for other combinations: drawn PP and isotropic LDPE or drawn LDPE and isotropic PP.

Detailed analysis of the temperature variations of the NMR spectra and their second moments7), together with the above stated results, concerning the $M_2(\vartheta)$ anisotropy, show that the combination of drawn LDPE and isotropic PP is most suitable for fitting the NMR experiments for drawn PP/LDPE blend. However, a more realistic model for drawn PP/LDPE blend must permit some degree of orientation of PP component. Our preliminary results, based on the analysis of the shape of the NMR spectra, support the simplified model for the investigated PP/LDPE blend, which consists of immiscible components PP and LDPE. When this isotropic blend is cold-drawn, up to reaching a complete necking ($\lambda \approx 4.5$), the LDPE component is drawn and oriented more effectively than the PP component. The total orientation of the sample is lower, when compared with the homopolymers drawn to the same degree.

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