

BROAD LINE NMR STUDY OF MACROMOLECULAR ORIENTATION IN ULTIMATELY DRAWN POLYPROPYLENE-POLYETHYLENE BLENDS

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SUMMARY

The macromolecular orientation in ultimately drawn tapes made of polypropylene-(low density) polyethylene (PP/PE) blends with different concentration of components has been studied by broad-line nuclear magnetic resonance (NMR). The dependences of the second moment of NMR spectra measured at ambient temperature have been analysed according to theoretical relationship derived for uniaxially oriented polymeric films or tapes. The parameters A_2 and A_4 characterizing the anisotropy and parameter A_0 characterizing the total second moment have been obtained for all studied tapes. It was found out that the tapes possess high degree of uniaxial macromolecular orientation.

A new parameter, χ , defined as a linear combination of anisotropy parameters A_2 and A_4 has been introduced. A constant value of this parameter for all samples suggests that the macromolecular orientation of PP and PE components in each blend is the same as it is in homopolymers alone, subjected to the same deformation conditions as blends. It means that the orientation obeys additivity rule. The immiscibility of components of PP/PE blends does not mean their absolute independency. Both components have to be „mechanically“ bound together. The partial amorphisation of the components in some blends has been deduced from parameter A_0 in the NMR second moment.

Keywords: polymer blends, polypropylene, polyethylene, macromolecular orientation, NMR, uniaxial deformation.

1. INTRODUCTION

It is well known [1, 2, 3] that the solid state physical properties of polymers are strongly influenced by the detailed arrangement of the constituent molecules. The solid state organization is characterized by the orientation of the polymer chains, by the degree and nature of the crystallinity and by the amount of noncrystalline or amorphous material. In the case of bicomponent (as well as multicomponent) polymer blends this macromolecular orientation is more complicated than in homopolymers, which constitute a particular blend.

Beside the intrinsic chemical and physical properties of component polymers the properties of blends depend strongly on concentrations as well as on processing conditions to which the material has been subjected. Materials with high degree of macromolecular orientation are often prepared by uniaxial or biaxial stretching. The basic mechanical parameters – tensile modulus and tensile strength depend primarily on stretching ratio λ ($\lambda = l/l_0$) for uniaxially drawn fibres, films or tapes [4, 5]. The greater is the stretching ratio, the greater is macromolecular orientation and modulus and strength. Thus it is very important to understand the nature of molecular orientation that can be introduced during the processing of molten polymers and of effects of this orientation on the mechanical and other physical properties of the solid material.

The macromolecular orientation can be studied experimentally by several methods, including X-ray scattering, birefringence, infrared dichroism and

mechanical measurements [1, 3]. As far as spectroscopy is concerned, nuclear magnetic resonance (NMR) is by its very nature sensitive to the chemical as well as physical structures, morphology, orientation, order and macromolecular chain dynamics. Various NMR techniques (pulsed and continuous) can provide complementary and additional information to that obtained by other methods [6].

The purpose of the present work is the characterization of macromolecular orientation in Polypropylene/Polyethylene tapes, uniaxially drawn, up to their break. Non-destructive parts of tapes were studied by broad-line NMR (BL-NMR). The analysis of the shapes of the NMR spectra and their second moments provide quantitative parameters characterizing the phase structure and orientation in a set of PP/PE blends with different contents of PP and PE. The only mean or overall orientation of macromolecules may be obtained from anisotropy of NMR second moment calculated from BL-spectra. This work follows our previous ones [7, 8, 9] where a particular PP/PE (70:30) blend with draw ratio $\lambda = 4.5$ has been studied.

2. CHARACTERIZATION OF SAMPLES AND EXPERIMENTAL CONDITIONS

Isotactic PP (PPTF 311, produced by Slovnaft, Bratislava) and a low density polyethylene (PE Bralen RA2-63 – Slovnaft) have been used as homopolymers for preparing blends with following compositions: 90PP/10PE, 70PP/30PE, 50PP/50PE, 30PP/70PE, and 10PP/90PE; the numbers at

polymer symbols present the weight per-cents of the corresponding component. The components were mixed together in a Brabender Plastrecorder at temperature of 190°C and the tapes were prepared by compression moulding at 190°C. Drawn tapes were prepared by means of an Instron testing equipment at room temperature (20-22°C) up to their fracture, with the clamps speed of 10mm/min.

A small rectangular strips cut from these tapes were stacked in a glass-tube attached to the sample-holder of the probe-head of NMR spectrometer. The probe-head includes a goniometer by which means the sample could be set at any angle to the applied magnetic field with an accuracy of about $\pm 2^\circ$.

NMR spectra in a derivative form were recorded by means of BL-NMR spectrometer operating at the proton (H^1) resonance frequency of 14.1MHz at ambient temperature. The second moment was calculated for each NMR spectrum by measuring the signal intensity at a small intervals (approx. $0.2G=2 \times 10^{-5}T$) from the center of resonance. The second moments were determined from experimental spectra with the accuracy better than $\pm 0.3 \times 10^{-8}T^2$.

3. THEORETICAL BACKGROUND

The starting point for a quantitative description of macromolecular orientation by means of NMR is the fact that the shape of the proton resonance line in a solid sample results from the distribution of local fields due to the surrounding magnetic nuclei around each proton of the system. For each pair of protons the dipolar field interaction is proportional to $(3\cos^2\beta_{jk} - 1)r_{jk}^{-3}$, where β_{jk} is the angle of the interproton vector \mathbf{r}_{jk} with the external magnetic field induction \mathbf{B} . In oriented polymers there exists certain distribution of linear segments of macromolecules which determines also the distribution of proton pairs with respect to angles β and the line shape is related to this distribution. Because of many-body character of the dipolar interaction the direct relation between the line shape and macromolecular orientation was not found. However, the moments of the line can be related to the structural parameters by the Van Vleck expressions [10, 11].

For the second moment, one has:

$$M_2 = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{G}{N} \sum_{j,k} r_{jk}^{-6} (3\cos^2\beta_{jk} - 1)^2 \quad (1)$$

where $G = I(I+1)\gamma^2$, I is the nuclear spin number ($I = 1/2$ for protons), γ - is the gyromagnetic ratio of resonating nuclei ($\gamma = 2.675123 \times 10^8 T^{-1}s^{-1}$), N - is the number of protons over which the sum is taken.

For uniaxially oriented sample with isotropic transversal distribution of macromolecular chains the expression for M_2 may be written in two equivalent forms [12, 13]

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

and

$$M_2 = A_4 P_4(\cos \vartheta) + A_2 P_2(\cos \vartheta) + A_0 \quad (3)$$

where the form (2) is convenient for mathematical treatment of experimental angular dependence of second moment $M_2(\vartheta)$ and the form (3) for physical interpretation.

The coefficients A , B , C and A_4 , A_2 and A_0 are interrelated as follows:

$$A_4 = \frac{8}{35}A, \quad A_2 = \frac{4}{7}A + \frac{2}{3}B, \quad A_0 = \frac{1}{5}A + \frac{1}{3}B + C \quad (4)$$

One can establish that the coefficients A_4 and A_2 are proportional to the Hermann's orientational parameters f_4 and f_2 , respectively. These parameters of the n -th order are defined as a mean values of Legendre's polynomials of n -th order:

$$f_n = \langle P_n(\cos \alpha) \rangle = \int_0^{\frac{\pi}{2}} F(\alpha) P_n(\cos \alpha) \sin \alpha d\alpha \quad (5)$$

where $F(\alpha)$ is „unknown“ orientation distribution function (ODF) of macromolecular chains, α is the angle between a particular chain axis with respect to drawing direction and $P_n(x)$ is the Legendre's polynomial of the n -th order [11-13].

The coefficient, A_0 , corresponds to the isotropic value of the second moment. By means of parameters A_i it is possible to monitor the changes in the chain orientations but the absolute values concerning the orientational parameters f_2 and f_4 can only be inferred from additional information and assumptions concerning the structural heterogeneity, molecular structure of the chains and their mobility [11-13].

As a measure of anisotropy of the second moment and also of the overall macromolecular orientation, the values of the parameters A , B (or A_4 , A_2) may be taken from fitting experimental values of $M_2(\vartheta)$ according to equation (2).

4. RESULTS AND DISCUSSION

As it was shown in our previous papers [7-9] NMR spectra of drawn PP and LDPE tapes change their shape with respect to the angle ϑ between stretching direction and external magnetic field induction \mathbf{B} . The angular dependences of the NMR second moments, $M_2(\vartheta)$, for all studied samples are shown in Fig.1. The lines put through experimental points were obtained by fitting experimental data

according to expression (2), the values of parameters

A , B , C and A_4 , A_2 , A_0 are listed in Tab. 1.

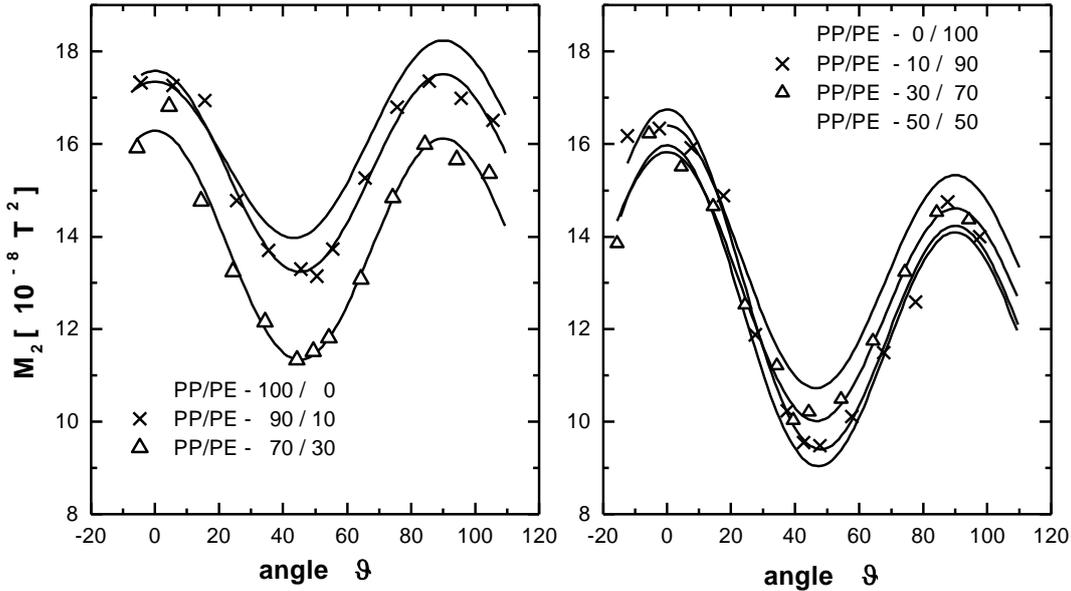


Fig.1: Angular dependences of the NMR second moment for PP/PE tapes with different wt.% of components.

The first step in analysis of our experimental results is to use the additivity principle [3] for NMR spectra and their second moments.

If the two components of the bicomponent blend were ideally separated each other or immiscible, the whole spectral function (in integral or differential form) would be expressed as a weighted sum of spectral functions of the corresponding homopolymers. In this case the same is valid also for second moments of these NMR spectra:

$$M_2 = w_{PP}M_{2PP} + (1 - w_{PP})M_{2PE} \quad (6)$$

where M_{2i} are the NMR second moments for homopolymers ($i = PP, PE$) and w_i are the relative numbers of resonating nuclei (H^1 nuclei in our case) in the homopolymers. For PP and PE blends the quantity w_{PP} is equal to weight fraction x_{PP} of the component (PP in our case).

However, the simple classification of blends into categories of miscible or immiscible, respectively, does not reflect the wide range of structures and properties covered. Immiscible blends (PP/PE are also the case) usually consist of a continuous matrix in which the second polymer is dispersed in a form of domains. The size of the domains and their adhesion to the matrix may differ significantly from one blend to other [14].

Some kinds of interactions of the components must exist even in immiscible blends, otherwise

properties (namely mechanical) become extremely poor. These not well defined interactions between components may be semiquantitatively evaluated also from the deviations of the NMR second moment values from those predicted by additivity rule. A closer packing of the polymer chains, increasing of their orientation and a reduction in their mobility would result in increase of second moment of the blend and vice versa.

As a quantitative measure of the inter-component interaction we define quantity ΔM_2 :

$$\Delta M_2 = x_{PP}M_{2PP} + (1 - x_{PP})M_{2PE} - M_{2BL} \quad (7)$$

where M_{2BL} is the second moment for blend at given conditions (given temperature or angle θ).

The same differences may be introduced for quantities A_4 , A_2 , A_0 (or A , B , C) which determine the anisotropy of the second moments according to relations (2) and (3).

The differences in quantities A_4 , A_2 and A_0 from additivity can be seen in Figures 2, 3. As we can see the experimental values of parameters, A_2 and A_4 , roughly follow the lines which connect the corresponding values for homopolymers. If we take into account that these parameters are estimated experimentally with an uncertainty of about 2% for all samples, the values of A_2 and A_4 may be analytically expressed as a linear functions in respect to concentration (x_{PP}) of the components.

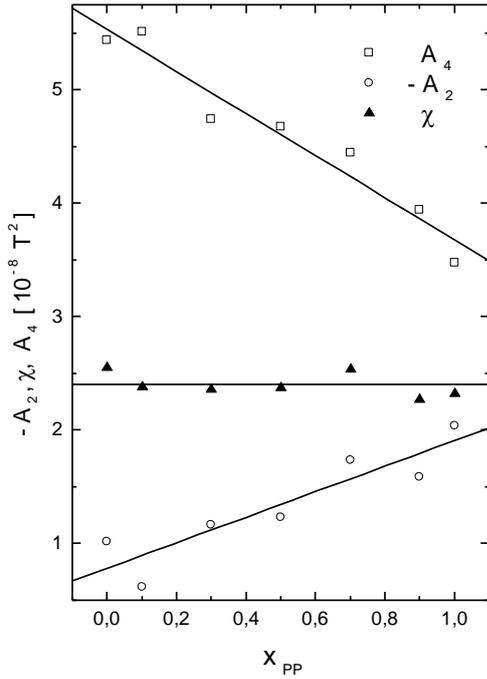


Fig.2: The concentration dependence of parameters A_4 , A_2 and χ for PP/PE tapes.

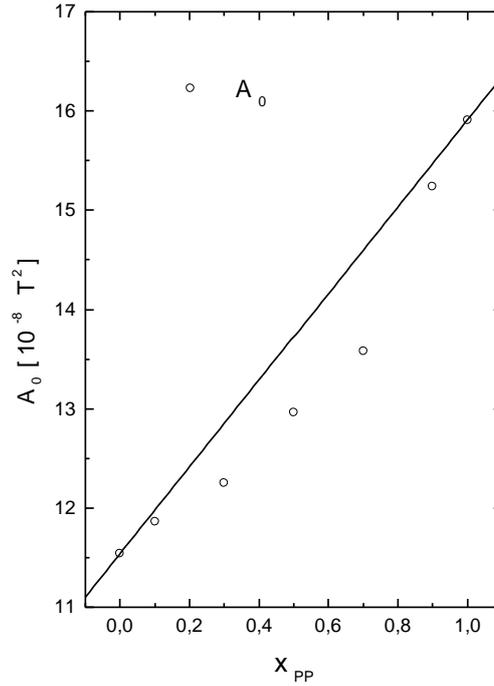


Fig.3: The concentration dependence of parameter A_0 for PP/PE tapes.

Despite of the concentration dependence of parameters A_4 and A_2 we have find that their linear combination, χ , defined as:

$$\chi = \frac{3}{8} A_4 - \frac{1}{2} A_2 \quad (8)$$

is practically independent of concentration and its value is $\chi = 2.40 \times 10^{-8} \text{ T}^2$. This value represents the difference between second moment at the angle of $\vartheta = 90^\circ$ and isotropic value of sample $M_{2is} = A_0$.

PP/PE Compos.	A	-B	C	A_4	$-A_2$	A_0	χ
100/0	15.24	16.13	18.24	3.48	2.04	15.91	2.32
90/10	17.26	17.18	17.51	3.94	1.59	15.24	2.27
70/30	19.47	19.30	16.12	4.45	1.74	13.58	2.54
50/50	20.49	19.41	15.33	4.68	1.23	12.96	2.37
30/70	20.73	19.52	14.61	4.74	1.17	12.25	2.36
10/90	24.11	21.59	14.23	5.51	0.62	11.86	2.38
0/100	23.82	21.94	14.09	5.44	1.02	11.54	2.55

Tab.1: Parameters characterizing the anisotropy of the NMR second moment, $M_2(\vartheta)$, for ultimately drawn tapes of PP/PE blends (in 10^{-8} T^2 units)

A linearity of the dependence of A_4 and A_2 on concentration of homopolymers points on the fact that the addition rule holds for ultimately drawn PP and PE and their blends in the whole range of concentration. In other words, the components in

the blend behave in the same manner as they behave when were deformed individually.

It can be stated that the additivity rule must not hold for others deformations where the responses of the components in a blend are different from the

responses of components subjected to the same drawing conditions. It was found also in our study of particular blend (70/30) drawn up to draw-ratio $\lambda = 4.5$ [7, 8, 9]. In that case PE component was highly oriented but PP one only in a small degree.

A higher deviations from additivity rule can be seen for parameter A_0 which is equal to isotropic value of the second moment (averaged out of $M_2(\mathcal{G})$ over all angles \mathcal{G}). A smaller values of A_0 for blends than those following from additivity suggest some kind of amorphisation of the blend as a consequence of the forming of crazes, cracks or voids during the destruction process. Destruction zones beside the highly oriented material contain also disordered material with loose packing of macromolecules and with higher mobility of the present chain ends of broken macromolecules.

5. CONCLUSION

The analysis of the angular dependences of the NMR second moments for a set of ultimately drawn PP/PE blends in a wide range of their compositions provides an important information on mean (overall) macromolecular orientation and on other changes in structure of the materials. It was found out that the parameters A_2 and A_4 which are directly proportional to the Hermann's orientational parameters, obey additivity principle and that there may be introduced a suitable parameter χ , which in this case is practically the same for all the samples (homopolymers and all their blends). It provides an experimental evidence that the macromolecular orientation of homopolymers in each blend is unaltered.

The isotropic part of the NMR second moment (A_0) deviates from the additivity, pointing on some kind of amorphisation of the blends with respect to homopolymers. Despite of the immiscibility of the components at least the „mechanical“ compatibility between them there must exist.

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