Temperature Variations of NMR Second Moments for Drawn Tapes Based on Polypropylene and Polyethylene

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Summary: Isotropic and drawn tapes prepared from isotactic polypropylene (PP), low density polyethylene (LDPE) and their blend PP/LDPE (70/30) have been studied by broad-line nuclear magnetic resonance (NMR) in the temperature range from 120 up to 320 K. The glass-transition temperatures, T_g, for studied samples have been determined from the temperature dependencies of the NMR second moments. It was found that the NMR spectra and their second moments are additive for isotropic blend in the whole temperature range, while a significant differences from addition rule appear for drawn PP/LDPE blend, when weighted average second moment is calculated by means of second moments of equally drawn homopolymers. It was found out that the LDPE component in the blend is drawn to a greater extent than PP component.

Introduction

The blending of polymers offers a possibility of tailoring of new technically important materials with specified physical properties. The macroscopic properties of the resulting blend are determined by microscopic and molecular factors like the degree of phase separation, the morphology, domain sizes, interfaces and the composition of the different phases. Further improvement of the polymer materials, including also blends, may be achieved by their plastic deformation. These deformations modify mechanical, optical and other physical properties. In the large majority of the uses of polymeric materials their mechanical properties are exploited primarily. Besides the macroscopical changes also the changes at microstructural level are caused by deformation. A variety of methods are available to investigate these changes, such as thermal analysis, the various forms of electron microscopy and X-ray scattering1). As far as spectroscopy is concerned, nuclear magnetic resonance (NMR) in the solid state offers important information about the structure, molecular order and mobility in polymer materials2-4). Materials based on polyethylene and polypropylene have been intensively studied also by various NMR solid-state techniques2-4).

CCC 1022-1360/00/$ 17.50+.50/0

This article deals with an analysis of the temperature dependencies of the second moments M_2 of NMR spectra, measured on a set of tapes prepared from isotactic polypropylene (PP), low density polyethylene (LDPE) and from their blend PP/LDPE with the weight fractions x_{PP}= 0.7 and x_{PE}= 0.3. The isotropic, as well as oriented tapes (unaxially stretched, with drawing ratio $\lambda \approx 4.5$) have been prepared from these materials. The temperature variations of NMR spectra and their second moments are analyzed to obtain information on thermally activated relaxation processes in a particular PP/LDPE blend and to find out how these processes are related to those in homopolymers.

Experimental

The samples in the form of tapes (approx. 1mm thick and 5mm wide) were prepared from isotactic polypropylene PPTF411 and from low density polyethylene LDPE-Bralen RA 2-19, both produced by Slovnaft (Bratislava, Slovak Republic). A similar samples were prepared from blend of PP and LDPE containing 70 wt% of PP and 30% of LDPE. The isotropic and cold-drawn (drawn at room temperature about 20-22 °C) tapes with draw ratio $\lambda \approx 4.5$ were investigated.

Basic parameters characterizing these polymers and more detailed information concerning the preparation procedures are stated in our paper5), presented in this journal.

The operating parameters of a broad-line NMR spectrometer were the same as those used in measurement of angular dependencies of the second moment5).

Samples for NMR measurements, prepared in the form of rectangular strips, 5mm wide and 20mm long, were stacked in a glass tube. Uniaxially drawn samples were placed in a probe head of spectrometer in such way, that the angle ϑ between the drawing direction and external magnetic field induction was kept 90°. NMR spectra were measured in the temperature range from about 120 K up to room temperature for undrawn samples and from approximately 200 K up to 310 or 400 K for drawn samples. The temperature intervals have been chosen to cover glass-transition regions, detected by NMR method.

Results and Discussion

The variations of the second moments M_2 with respect to temperature are shown in Fig.1 for all the samples. It is seen that in all cases temperature ranges exist where second moment decreases with increasing temperature. It indicates an existence of some motional processes causing a time averaging of the anisotropic magnetic dipole-dipole interactions between resonating nuclei, leading to a narrowing of NMR spectra. For polyethylene and polypropylene these variations are well known from literature[2-4], as well as from our investigations, devoted namely to polypropylene[6-7]. We shall comment our results concerning the homopolymers PP and LDPE only briefly, because main concern will be concentrated on their blend.

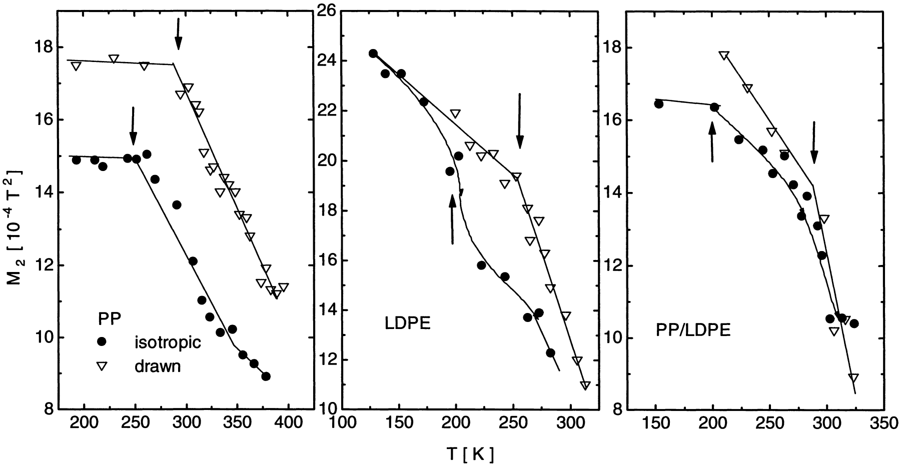

Fig.1. Temperature dependencies of the second moment for isotropic (undrawn, circles) and drawn (triangles) tapes.

Second moment for LDPE samples decreases gradually with increasing temperature in the whole experimental temperature interval. The initial decrease (at temperatures between 130 K and 180 K), common for isotropic material and for drawn tapes, is caused by so called γ-process[2]. At temperatures above 200 K the courses of $M_2(T)$ dependencies are different for undrawn and drawn samples. A sudden decrease of M_2 at temperatures between 180-210 K indicates an intensive motion of PE chains in noncrystalline regions, corresponding to so called β- relaxation in undrawn LDPE. These motions are closely related to a glass-transition, characterizing by the temperature T_g. Regarding a glass-transition temperature for this sample the value $T_g \approx 200$ K has been estimated. The glass-transition temperature for drawn LDPE can be derived from the intersection of lines representing different slopes of the $M_2(T)$ dependence, which coincides with temperature $T_g \approx 250$ K. Further decrease of M_2 for both polymers indicates an increase in both the intensity of molecular motions and a number of PE chains performing such motions. This effect is manifested by the presence of a narrow line in the NMR spectra, whose intensity increases with temperature.

A similar, but not identical changes in $M_2(T)$ dependencies may be observed for PP tapes. Plateaus of the M_2 with a nearly constant values of $M_2 \approx 15.3\text{x}10^{-8}\ T^2$ below 250 K and $M_2 \approx 17.5\text{x}10^{-8}\ T^2$ below 290 K are characteristic for isotropic and drawn PP, respectively. The glass-transition temperatures of $T_g \approx 260$ K and $T_g \approx 290$ K may be determined from $M_2(T)$ dependencies. These dependencies have been analyzed in our paper[8)], where the activation energies for β-process were determined to be W_a= 30.4 kJ/mole for isotropic and W_a= 27.1 kJ/mole for drawn PP, respectively.

The temperature dependencies $M_2(T)$ for PP/LDPE samples have some typical features of both homopolymers. There is a hint of a decrease of M_2 at temperatures close to 200 K and a significant decrease at temperatures above 250 K for undrawn blend. Two T_g's may be ascribed for this sample: a "lower" $T_{g1} \approx 200$ K – corresponding to isotropic LDPE component and an "upper" one at $T_{g2} \approx 250$ K, corresponding to the isotropic PP component.

A behavior of the $M_2(T)$ dependence for drawn blend is somewhat different. The second moment decreases gradually with increasing temperature up to ≈ 290 K, with the slope characteristic for decrease of M_2 for drawn LDPE up to it's $T_g \approx 250$ K, and then decreases more rapidly. This temperature (290 K) is assumed to be T_g for drawn PP.

The glass-transition temperatures determined from $M_2(T)$ dependencies are listed in Tab.1. The values are determined with an uncertainty of about ±10 K.

The NMR experiments provide also a test of miscibility or immiscibility of components in a polymer blend. As a measure for this test, a difference, ΔM_2, defined as:

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

may be accepted, where x_{PP} is the mass-fraction of PP component (x_{PP}= 0.7) in a two-component blend, M_{2PP}, M_{2PE} and M_{2BL} are corresponding second moments for PP, LDPE and their blend (BL), respectively.

Table 1. Glass-transition temperature obtained from $M_2(T)$ dependencies.

	Tg / K					
Sample	LDPE	LDPE	PP	PP	PP/LDPE	PP/LDPE
	isotr.	drawn	isotr.	drawn	isotr.	drawn
PE component	200	250			200	-
PP component			260	290	250	290

Using the corresponding values for second moments, measured at the same temperature, these differences (from addition rule) have been calculated. Some of the M_2 values were obtained from experimental dependencies $M_2(T)$ by means of an interpolation. These differences for undrawn and drawn samples are shown in Fig.2. As we can see, the differences ΔM_2 for isotropic blend oscillate around zero, indicating that the PP and LDPE components may be assumed as independent, so that this blend is immiscible. However, if we apply the same procedure for drawn blend with the second moments for equally drawn homopolymers, nonzero, positive and temperature dependent differences are obtained (see Fig.2). It is due to the fact that in the nearly whole experimental temperature range the second moments for drawn blend have smaller values than those for the drawn homopolymers.

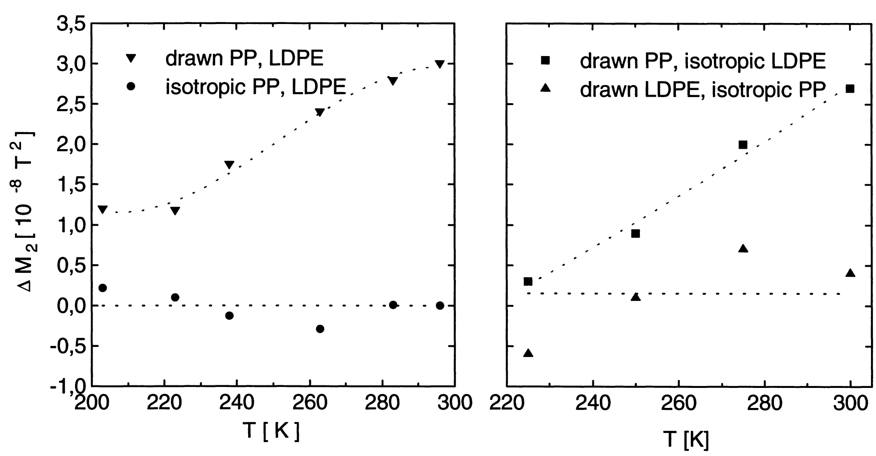

Fig.2. Temperature dependencies of ΔM_2 [according to (1)] in the LDPE / PP blend, considering four possible limiting cases: both components drawn or isotropic (left), one component drawn another isotropic (right).

Some important information about changes caused by stretching of an isotropic blend up to a given draw ratio $\lambda \approx 4.5$ may be obtained from more detailed investigation of the course of $M_2(T)$ dependence for drawn blend in comparison with the analogous dependencies for the other samples. As we can see from Fig.1, the greater values of $M_2(T)$ are observed for drawn blend than those for undrawn mixture at temperatures $T \leq 260$ K. It may be accounted for as an effect of macromolecular orientation in drawn blend. The molecular motions in PE domains are not still effective to create narrow NMR line, but they are manifested by the decrease of the second moment with rising temperature (from 200 to 260 K), similarly as it is for drawn LDPE sample. The narrow spectral line for individual samples becomes visible at temperatures higher than corresponding T_g's (listed in Tab.1).

Smaller differences (≈ $1x10^{-8}$ T^2) of the M_2 values for drawn and undrawn blends are observed at higher temperatures, between 260 and 300 K.

However, much larger differences (≈ $4\div5x10^{-8}$ T^2) have been observed between second moments of drawn and undrawn homopolymers. Therefore it is suggested that the degree of macromolecular orientation is higher in drawn homopolymers that in drawn blend, although the materials were stretched to the same extent. The narrow spectral line, indicating a micro-Brownian motions[9)] with growing intensity, appears at these temperatures for all samples, with exception of PP.

Up to now, almost all features concerning the changes in NMR spectra and their second moments, for PP/LDPE blends, may be accounted for as the corresponding changes in NMR spectra of LDPE. It is not surprising, bearing in mind that T_g for PP homopolymers are significantly higher than T_g of LDPE. The narrowing of the NMR spectra for PP occurs at temperatures higher than T_g and a visually observed narrow lines appear above room temperature. When the isotropic PP/LDPE is drawn at room temperature, the PP component remains more or less glassy with a great resistance against mechanical stress imposed, but the LDPE component possesses well-developed visco-elastic properties and its deformation is easier than that of PP. Hence, a higher degree of macromolecular orientation in LDPE component would be expected compared to PP component in the blend.

Now we are able to give, at least qualitatively, a reason for observed deviations of ΔM_2 from addition rule for drawn PP/LDPE blend compared to drawn homopolymers. Our NMR measurements clearly suggest different responses to drawing of the components in blend in comparison with those in homopolymers alone.

An approximate model for our PP/LDPE blend may be proposed on the basis of discussion outlined above, which assumes that LDPE component in the blend is oriented to a similar degree as drawn LDPE while PP component remains nearly isotropic. Taking the corresponding values of $M_2(T)$ (from Fig.1) the differences $\Delta M_2(T)$ may be calculated. As we can see from Fig.2 these differences are much less than those for drawn homopolymers and for combination drawn PP and isotropic LDPE.

It could be naturally expected, that PP component in blend is also drawn, in some extent, but less than LDPE component.

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