Broad Line $^1$H NMR Studies of Glass Transition Relaxation Process in Drawn Samples of Polypropylene/EPDM Blend

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Abstract: Samples of the isotactic polypropylene (i-PP) and polymer blend composed of i-PP and ethylene-propylene-diene monomer rubber (EPDM) have been studied using the broad-line $^1$H NMR. The NMR measurements were performed on the plate form samples of undrawn and drawn i-PP and on the samples of the polymer blend in the temperature range 200 – 370 K. The effect of drawing and the effect of drawing temperature on relaxation processes related to the glass transition of both polymers were studied. Drawing results in the increase of chain mobility in i-PP samples as can be deduced from the temperature dependences of the second moment and parameters derived from decomposition of the NMR spectra. A double glass transition was observed in the i-PP/EPDM blend.

Keywords: Glass transition temperature, isotactic polypropylene, ethylene-propylene-diene terpolymer, drawing, broad-line $^1$H-NMR.

1. INTRODUCTION

Isotactic polypropylene is considered to be a three-phase system with amorphous, intermediate, and crystalline regions. The blending of i-PP with the amorphous EPDM results in an additional phase within the system [1]. The molecular processes in the i-PP, EPDM rubber and in the blend composed of i-PP and EPDM rubber (i-PP/EPDM) were investigated in more previous works [2-5]. In this paper the effects of drawing and drawing temperature on relaxation process related to the glass transition of i-PP and i-PP/EPDM blend are studied.

2. EXPERIMENTAL

The broad-line $^1$H NMR experiments were carried out on drawn and undrawn samples of i-PP and i-PP/EPDM blend containing 22.5 % of the terpolymer. The drawing of samples prepared in the form of plates with thickness of 2 mm and width of 5 mm was done at the temperatures 23 °C and 100 °C. The maximum reachable draw ratio for both samples was about 3.5. Both drawn and undrawn plates were cut into small pieces to prepare non-oriented samples for NMR measurements. The glass transition temperatures of the i-PP and EPDM rubber are 270 K and 218 K, respectively [2].

The broad line $^1$H NMR measurements were performed with the continuous wave spectrometer which operates at the fixed magnetic field $B_0 = 0.247$ T using frequency sweep through resonance region [6]. The NMR measurements were carried out in the temperature range 200 – 370 K.

3. RESULTS

The broad line NMR spectrum measured on the partially crystalline polymers can be expressed as the superposition of the elementary spectra $y_n, y_m, y_b$, which are related to the amorphous (micro Brownian motion), intermediate (hindered motion) and crystalline (rigid chains) regions, respectively [7]. Usually, the narrow component $y_n$ is the Lorentzian function, the middle one $y_m$ is the product of the Gaussian and Lorentzian functions and the broad elementary spectrum $y_b$ is derived from the measured low temperature spectrum. The calculated spectrum $y_c$ can be expressed in terms of the elementary spectra $y_n, y_m, y_b$ by the equation

$$
y_c = w_n y_n (\Delta B, \beta_n, B_{mod}) + w_m y_m (\Delta B, \beta_m^L, \beta_m^G, B_{mod}) + w_b y_b (\Delta B, S)
$$

where $\Delta B = B - B_0$ is the difference between the applied magnetic field $B$ and the resonance magnetic field $B_0$. The relative mass fractions $w_i$, parameters $\beta_i$ (i = n, m, b) and parameter $S$ are related to the amorphous (n), intermediate (m) and crystalline (b, S) chains.

The influence of the modulation field, that was $B_{mod} = 0.22 \times 10^{-6}$ T, on the narrow elementary spectrum was considered. Elementary spectra $y_i(x)$ as well as the whole spectral function $y_c(x)$ are normalized to unity, so the following relation holds: $w_n + w_m + w_b = 1$. All parameters $w_i, \beta_i$ and $S$ were obtained by the least square method [6].

The mass fractions $w_i$ estimated from the spectrum at the given temperature determine the fractions of the chains undergoing the micro Brownian motion ($w_n$), hindered motion ($w_m$) and rigid chains ($w_b$). All chains of both the crystalline and non-crystalline regions are considered to be rigid below the glass transition temperature as the mass fraction $w_b = 1$. A drop of this value to 0.65 is observed in the temperature range 275 – 325 K in the case i-PP (Fig. 1). It is reasonable to assume that molecular motion is activated within all non-crystalline domains at the temperatures far above $T_g$ and to consider the value 0.65 ± 0.02 as the crystallinity of the i-PP sample.
The decreases of the mass fraction $w_b$ for both drawn i-PP samples occur in the temperature range 260 – 325 K (Fig. 1). At the temperatures above 325 K the mass fraction $w_b$ take on the values 0.65 ± 0.02 and 0.60 ± 0.02 related to pp100 and pp23, respectively. We consider these values as crystallinities of the drawn i-PP samples.

In the case of all discussed i-PP samples the decrease of the mass fraction $w_b$ is observed at the expense of the increases of the mass fractions $w_m$ and $w_n$ (Fig. 1). At the temperature range above 320 K the lower values of $w_n$ related to drawn i-PP can be observed in comparison with those related to the undrawn i-PP and, on the other hand, the higher values of $w_m$ in the temperature range 300 – 370 K are observed in the case of drawn samples. Behaviour of the mass fractions $w_m$ and $w_n$ described above can be explained by the known fact that drawing gives rise to increased orientation and to tightening of macromolecules and so to restriction of chain mobility [8].

Fig. (2) shows the temperature dependences of the second moment $M_2$ related to samples of pp, pp23 and pp100 in the temperature range of the glass transition. In the temperature range 250 – 290 K the second moment values $M_2$ for drawn pp23 and pp100 samples are lower than that of the undrawn sample. The same conclusion can be drawn from the temperature dependences of the second moment $M_2$ depicted in Fig. (4). The temperature dependences of the second moment $M_2$ of the NMR spectra measured on i-PP/EPDM samples differ from those depicted in Fig. (2) for i-PP samples. In the case of both the undrawn and drawn i-PP/EPDM samples the second moment $M_2$ decreases continuously up to 320 K with the exception of the narrow temperature region within 270 - 290 K where a small plateau that separates temperature regions related to different relaxation processes is observed.
Consequently, the mass fractions estimated from the spectra measured in the range 340 – 360 K determine crystallinity and the relative fractions of the chains in amorphous and intermediate regions which in the i-PP and i-PP/EPDM samples differ markedly as can be seen in Figs. (1 and 3).

4. CONCLUSIONS

The broad line $^1$H NMR spectra were measured on the plate-shaped samples of i-PP and i-PP/EPDM blend in the broad temperature range that covers the glass transition relaxation processes in i-PP and EPDM rubber. The second moment $M_2$ data and parameters obtained from the decomposition of the NMR spectra were used to explain the effect of the drawing performed under different temperatures on the relaxation processes associated with the glass transitions of the investigated materials.

The chain mobility increase in i-PP as a consequence of drawing was inferred from both the temperature dependences of the second moment $M_2$ and mass fractions related to the polymer domains with different chain mobility. The drawing of the i-PP made under different temperatures results in the change of the mass fractions. The lower mass fraction of the chains performing micro Brownian motion in the i-PP drawn at 100 °C as compared with the mass fractions estimated for i-PP drawn at 23 °C was found.

In the case of the i-PP/EPDM blend the temperature dependences of the second moment $M_2$ and mass fractions $w_i$ differ greatly from those obtained on the i-PP samples. The double glass transition deduced from the courses of the temperature dependences provides evidence that polymer blend includes structure consisting of pure EPDM rubber domains. Evidently, in spite of the amorphous character of the EPDM rubber the higher amount of the intermediate chains was found in the i-PP/EPDM blend than in the i-PP samples.

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REFERENCES
