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

J. Onufer*, O. Fričová, Ľ. Mucha and D. Olčák

Department of Physic, Faculty of Electrical Engineering and Informatics, Technical University of Košice, Letná 9, 042 00 Košice, Slovak Republic

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 transitions 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.

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

$$y_c = w_n\, y_n\,(\Delta B, \beta_n^L, B_{\mathrm{mod}}) +$$
$$w_m\, y_m(\Delta B, \beta_m^L, \beta_m^G) + w_b\, y_b(\Delta B, S) \qquad (1)$$

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 β_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} = 0.22x10^{-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, β_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.

*Address correspondence to this author at the Department of Physic, Faculty of Electrical Engineering and Informatics, Technical University of Košice, Letná 9, 042 00 Košice, Slovak Republic; Tel: 055/602 2760; E-mail: jozef.onufer@tuke.sk
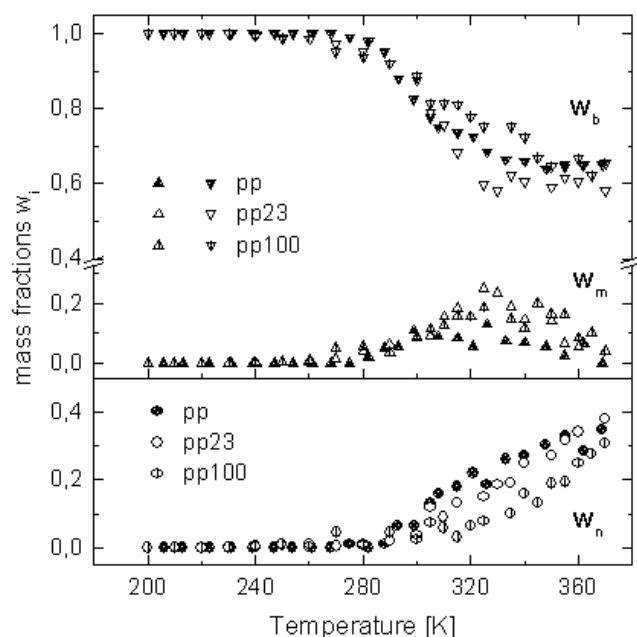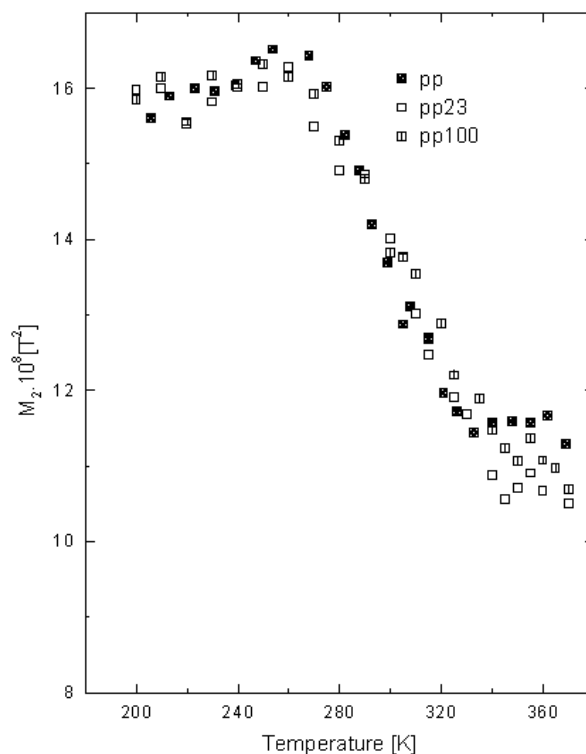
Fig. (1). Temperature dependences of the mass fractions w_n (●), w_m (▲), w_b (▼) related to the undrawn sample (denoted as pp) and to the samples drawn at temperatures 23 °C (pp23) and 100 °C (pp100).

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. In the same temperature range the drawn samples exhibit little lower mass fractions of the w_b when compared with the undrawn sample. Both results indicate higher chain mobility in drawn samples when compared with undrawn i-PP that, as it was reported in [9], can be a consequence of the free volume increase caused by the drawing.

Behaviour of the temperature dependences of both the mass fractions w_i and second moment M_2 estimated from the spectra measured on the polymer blend differ from those measured on the i-PP. The decrease of the mass fraction w_b within the broad temperature range reveals the existence of
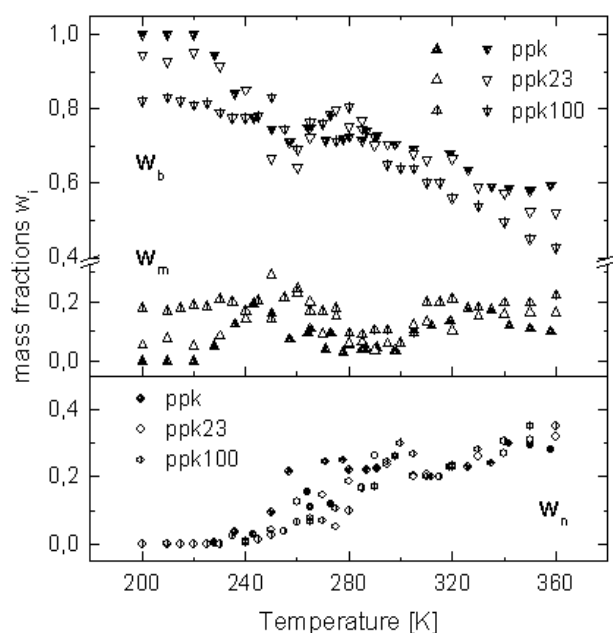

Fig. (2). The temperature dependences of the second moment M_2 of the spectra measured on the undrawn sample of the i-PP (pp), the drawn i-PP at the temperature 23 °C (pp23) and 100 °C (pp100).

two distinct relaxation processes (Fig. **3**). The temperature regions in which the different decreases of the mass fraction w_b are observed correspond to the temperature regions of the glass transitions of the particular components of the blend. This indicates that the components of the blend are miscible only to a certain degree and the polymer blend under study contains also net domains of the EPDM rubber [10]. 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.

The temperature dependences of the mass fraction w_m show that molecular motions in noncrystalline regions of i-PP/EPDM in contrast with i-PP are excited within the whole detected temperature range. The complicated temperature dependences of the fractions w_m and w_n reflect relaxation processes associated with the double glass transition in i-PP/EPDM blend.

As we could see, the mass fractions w_i that are determined on the bases of the different kind of motions in particular phases of the polymer, depend not only on the structure but also on the temperature. However, it is reasonable to assume that the micro-Brownian motion in amorphous regions and hindered chain motion in intermediate regions are completely excited in the temperature region above 340 K.

Fig. (3). Temperature dependences of the mass fractions w_n (●), w_m (▲), w_b (▼) related to the undrawn sample of the i-PP/EPDM (ppk), the drawn i-PP/EPDM at the temperature 23 °C (ppk23) and 100 °C (ppk100).
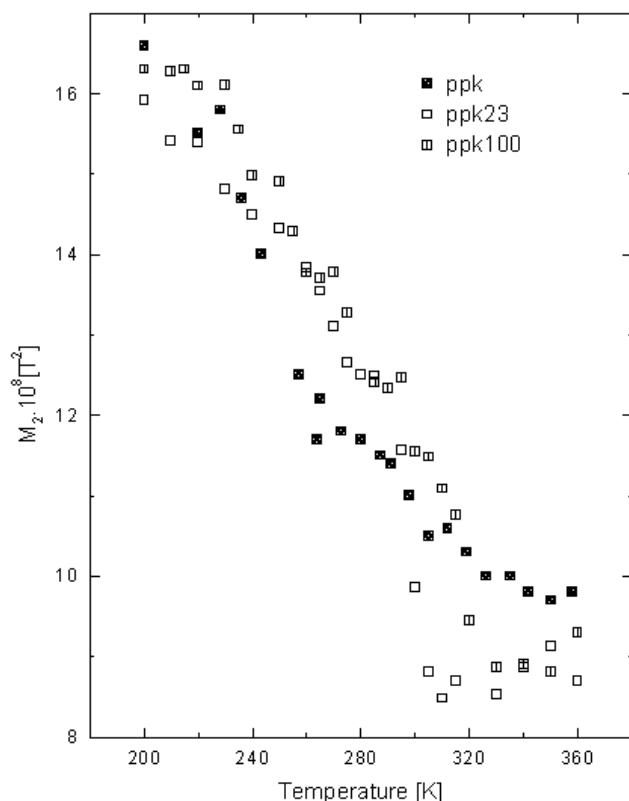
Fig. (4). The temperature dependences of the second moment M_2 of the spectra measured on the undrawn sample of the i-PP/EPDM (ppk), the drawn i-PP/EPDM at the temperature 23 °C (ppk23) and 100 °C (ppk100).

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.

ACKNOWLEDGEMENTS

REFERENCES

[1] Olčák, D.; Mucha, Ľ.; Onufer, J.; Raab, M.; Spěváček, J. Broad line ^{1}H NMR study of polymer blends composed of isotactic poly-propylene and ethylene-propylene-diene terpolymer. *Acta Electrotechn. Inform.*, **2002**, *2*, 31-35.

[2] Olčák, D.; Onufer, J.; Mucha, Ľ.; Raab, M.; Spěváček, J. Study of motional processes in polymer blends composed of isotactic poly-propylene and ethylene-propylene-diene monomer rubber by broad-line ^{1}H-NMR. *J. Appl. Polym. Sci.*, **2004**, *91*, 247-252.

[3] Bergmann, K. Study of the molecular motions of polyethylene by line-shape analysis of broad-line proton NMR spectra. *J. Polym. Sci., Polym. Phys. Ed.*, **1978**, *16*, 1611-1634.

[4] Hedesiu, C.; Demco, D. E.; Remerie, K.; Blumich, B.; Litvinov, V. M. Study of uniaxially stretched isotactic poly(propylene) by ^{1}H solid-state NMR and IR spectroscopy. *Macromol. Chem. Phys.*, **2008**, *209*, 734-745.

[5] Litvinov, V.M. EPDM/PP thermoplastic vulcanizates as studied by proton NMR relaxation: Phase composition, molecular mobility, network structure in the rubbery phase, and network heterogeneity. *Macromolecules*, **2006**, *39*, 8727-8741.

[6] Ševčovič, L. An improved CW NMR broad-line spectrometer for weak signal detection. *Acta Electrotechnol. Inform.*, **2006**, *4*, 43-46.

[7] Uhrin, J.; Murín, J.; Olčák, D. A modification of Bergmann`s method of the decomposition NMR spectra of polymers. *Acta Phys. Slovaca*, **1984**, *34*, 209-216..

[8] De Candia, F.; Botta, A.; Vittoria, V. The effect of drawing on the glass transition of quenched isotactic polypropylene**.** *J. Polym. Sci., Polym. Phys. Ed.*, **1986**, *24*, 2145-2148.

[9]   Fričová, O.; Olčák, D.; Ševčovič, L.; Ďurčová, O. NMR and dynamic mechanical studies of drawn polypropylene fibers. *Acta Polymer*, **1998**, *49*, 495-501.

[10]   Xiao, H.W.; Huang, S.Q.; Jiang, T.; Cheng, S.Y. Miscibility of blends of ethylene-propylene-diene terpolymer and polypropylene. *J. Appl. Polym. Sci.*, **2002**, *83*, 315-322.