

Study of Motional Processes in Polymer Blends Composed of Isotactic Polypropylene and Ethylene–Propylene–Diene Monomer Rubber by Broad-Line ^1H -NMR

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Received 16 October 2002; accepted 9 May 2003

ABSTRACT: The broad-line ^1H -NMR study of the polymer blend composed of isotactic polypropylene and ethylene–propylene–diene monomer rubber was carried out. The NMR measurements were performed on the samples of the polymer blend and on the components of the blend in the temperature range covering the glass-transition regions of all studied polymers. Conclusions were drawn from the temperature dependencies of the second moment M_2 and of the data obtained by the decomposition of the spectra into the components related to the motionally distinct regions of the partially crystalline polymer. The mass fractions of the amorphous, intermediate, and crystalline domains and the widths of the spectra related to the particular phases were computed from the spectra. A double glass transition was

revealed for the polymer blend. Different mechanisms of the motional processes related to the glass transition were deduced from the data. The gradual increase of the number of the chains and the enhancement of the chain mobility within noncrystalline regions of the polymer blend are responsible for the motion related to the lower glass transition and only transformation of the hindered motion into free motion was found in the temperature region of the upper glass transition. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 247–252, 2004

Key words: isotactic polypropylene (*i*-PP); EPDM rubber; blends; glass transition; broad-line ^1H -NMR

INTRODUCTION

Isotactic polypropylene (*i*-PP) is a fundamental stereoregular polymer with a stable helical chain conformation and glass-transition temperature $T_g \cong 270$ K. It has some excellent physical properties such as high stiffness, tensile strength, and reasonably high melting temperature (~ 435 K), although, on the other hand, the low-temperature performance of polypropylene is limited because of the relatively high glass transition. It is known to have poor impact strength and is brittle at low temperatures. It has been found that blending with a suitable ethylene–propylene rubber as a minor component can decrease the brittle transition temperature and considerably enhance the low-temperature toughness.^{1–3}

Macroscopic properties of polypropylene-derived blends can be predicted from the knowledge of the

properties of the components and the structure of the blend. On the other hand, there is a close connection between the structure and molecular motions that are reliably detected by means of NMR. Broad-line ^1H -NMR has been extensively used for the study of the partially crystalline *i*-PP in the past (Olčák et al.⁴ and references therein) and it has been shown that analysis of the broad-line NMR spectrum provides information on the chain mobility and proportion of motionally distinct regions in the polymer system.

The *i*-PP is frequently interpreted as a three-phase system with amorphous, intermediate, and crystalline phases. The modification of the *i*-PP by the amorphous ethylene–propylene–diene monomer rubber (EPDM) will add an additional phase to the system. The aim of this study was to investigate the structural changes and motional processes in the blend composed of the *i*-PP and EPDM rubber (*i*-PP/EPDM blend) in the temperature region of the glass transition with the use of the broad-line ^1H -NMR.

EXPERIMENTAL

The broad-line ^1H -NMR experiments were carried out on samples of the *i*-PP, EPDM rubber, and on the blend prepared from these polymers.

The isotactic polypropylene was a commercial partially crystalline polymer Mosten 58.412 (supplied by

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Contract grant sponsor: Slovak Grant Agency; contract grant number: 1/7402/20.

Contract grant sponsor: Grant Agency of the Czech Republic; contract grant number: 106/02/1249.

Contract grant sponsor: Grant Agency of the Academy of Sciences of the Czech Republic; contract grant number: KSK4050111.

Chemopetrol Litvínov, Czech Republic). The density of the polymer, determined by the flotation technique, was $\rho = 899 \text{ kg m}^{-3}$. The crystallinity of the sample was calculated by means of the density according to the formula

$$X_c = \frac{\rho}{\rho_c} \frac{\rho - \rho_a}{\rho_c - \rho_a} \quad (1)$$

in which ρ_c and ρ_a are densities of the crystalline and amorphous domains, respectively; $X_c = 0.58$. The EPDM rubber Keltan 512 (DSM, The Netherlands) was an amorphous copolymer of ethylene, propylene, and diene. It contained 55, 41, and 4% of carbon atoms in ethylene, propylene, and diene units, respectively, and its glass-transition temperature, as established by DSC, was 218 K. It was supplied as a bale, from which small pieces of about 2 cm in diameter were cut. The following facilities (of the Center of polyolefins of Slovnaft Bratislava, Slovakia) were used for the preparation of the homogeneous blend of these rubber pieces with polypropylene pellets (given in respective order): Banbury mixer, laboratory calender, knife mill, and double-screw extruder (Werner & Pfleiderer). The resulting blend in the form of pellets contained 22.5 wt % of the EPDM rubber and had a density of 892 kg m^{-3} . The pellets were finally processed into standard specimens for mechanical testing using an injection-molding machine (Battenfeld BA 750-200) in the Polymer Institute Brno, Czech Republic. Similarly, specimens of neat *i*-PP were prepared using injection molding. The conditions of injection molding were described elsewhere.⁵ The injection-molded specimens of the *i*-PP and *i*-PP/EPDM blend were cut into small pieces and inserted into glass tubes (10-mm diameter) for the NMR measurements.

The broad-line ^1H -NMR spectra were measured on the continuous wave spectrometer RJa 2301 (Russia) that operates at the resonant frequency $f_0 = 14.1 \text{ MHz}$ in the temperature range 160–370 K. The operating parameters of the spectrometer were the same within the whole temperature range. The sweep of the magnetic field $\Delta B/\Delta t = 10 \mu\text{T s}^{-1}$, the time constant of the phase detector $\tau = 1 \text{ s}$, the frequency of the sinusoidal modulating field $f_m = 35 \text{ Hz}$, and the amplitude of the field was $B_m = 1 \times 10^{-4} \text{ T}$.

RESULTS AND DISCUSSION

It is well known that the broad-line ^1H -NMR spectra measured on the motionally heterogeneous polymer system consist of several components related to the chains with different mobility. Because of the high sensitivity of the NMR spectra to molecular motions the distinct changes of the spectra measured on the partially crystalline *i*-PP in the glass-transition tem-

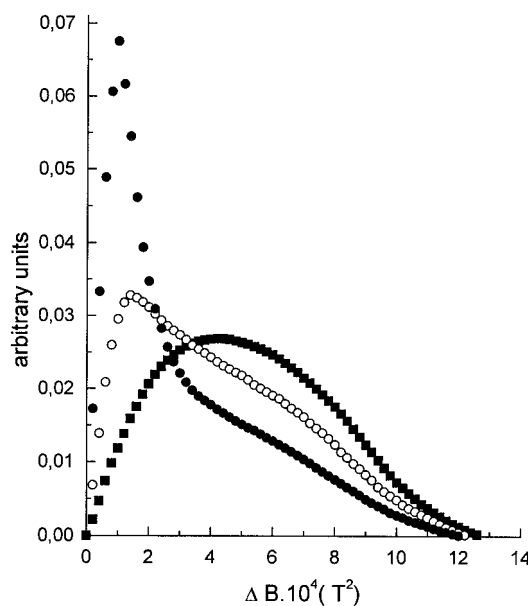


Figure 1 Derivations of the broad-line NMR absorptions measured on *i*-PP at temperatures 200 (■), 299 (○), and 333 K (●). Because of the symmetrical shape of the spectra only their halves are depicted.

perature region are observed in Figure 1. The broad structureless spectra are detected below the glass-transition temperature region that reflect the rigid chain structure within the crystalline and amorphous domains, whereas the spectra composed of the broad and narrow lines are observed above the mentioned temperature region. The broad line of the spectra is related to the rigid crystalline chains and the narrow line arises from the mobile chain segments in the amorphous regions. However, an analysis of the broad-line NMR spectra has shown that the spectra measured on the partially crystalline polymers consist of three components that are related to the crystalline, intermediate, and amorphous chains. Bergmann et al.^{6–9} suggested that the broad-line NMR spectrum y_c can be expressed in terms of the narrow, middle, and broad elementary spectra, y_n , y_m , and y_b , respectively, according to the equation

$$y_c = w_n y_n(\Delta B, \beta_n^L, B_{\text{mod}}) + w_m y_m(\Delta B, \beta_m^L, \beta_m^G) + w_b y_b(\Delta B, S) \quad (2)$$

in which $\Delta B = B - B_0$ is a difference between the applied magnetic field induction B and the resonance magnetic field B_0 , and w_i ($i = n, m, b$) are the relative mass fractions related to the amorphous, intermediate, and crystalline chains, respectively. The narrow component y_n is described by the Lorentzian function, y_m is a product of the Lorentzian and Gaussian functions, and y_b was derived from the measured low-temperature spectrum. The β_i and S are parameters of the

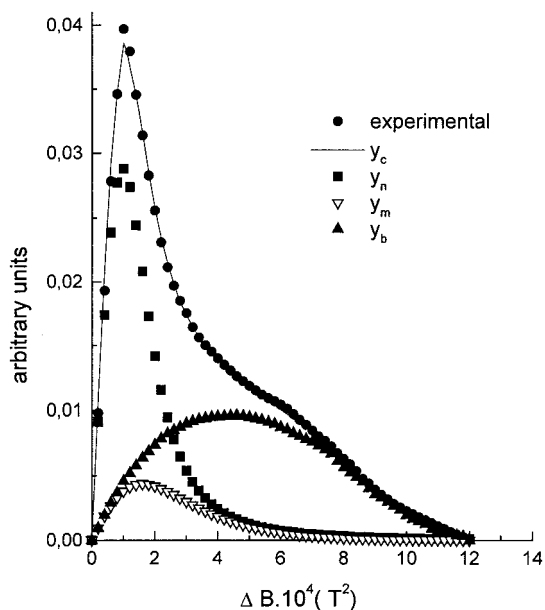


Figure 2 Decomposition of the NMR spectrum measured on *i*-PP at 321 K into elementary components as indicated. The computed parameters were as follows: $w_n = 0.23$, $w_m = 0.07$, $w_b = 0.70$, $\beta_n^L = 1.11 \times 10^{-4} T$, $\beta_m^L = 2.70 \times 10^{-4} T$, $\beta_m^G = 5.30 \times 10^{-4} T$, $S = 0.98$. The broad component y_b was derived from the low-temperature spectrum measured at 200 K depicted in Figure 1.

individual spectra. The β_n^L is related to the width of the narrow Lorentzian spectrum y_n , the β_m^L and β_m^G determine both the width and shape of the middle elementary spectrum y_m , and the scaling factor S describes a narrowing of the broad elementary spectrum y_b with respect to the low-temperature spectrum. The influence of the modulation field B_{mod} on the narrow elementary spectrum y_n was considered in our computation.¹⁰ The decomposition of the spectrum measured on *i*-PP at 321 K is shown in Figure 2. The broad component y_b of the spectrum was derived from the spectrum measured at 200 K, shown in Figure 1.

Before discussing the spectrum decomposition according to eq. (2), it would be useful to introduce some substantial features of the temperature dependencies of the second moment M_2 . It is known that the second moment M_2 of the ^1H -NMR spectrum depends on both the spatial configuration of hydrogen protons and their motions.

The temperature dependencies of the second moment M_2 calculated from the NMR spectra measured on the *i*-PP, EPDM rubber, and *i*-PP/EPDM blend are depicted in Figure 3. In the case of *i*-PP the temperature dependency of the second moment M_2 agrees with results described in our previous studies.^{11,12} The second moment takes up the values of about $16 \times 10^{-4} \text{ T}^2$ at temperatures below 270 K. It is known that the CH_3 side-group rotations and rigid main chains are responsible for this value.^{13,14} A decrease of the sec-

ond moment, seen in the region 270–320 K, is related to the glass transition. The plateau above this temperature range shows that an excitation of the motion occurs within the whole noncrystalline part of PP.

In the temperature dependency of second moment M_2 for EPDM a two-step decrease is observed: a slower one from about 160 to about 220 K and a faster one above this temperature. Apparently, the distinct decrease observed up to 250 K can be associated only with the glass transition of the EPDM rubber. With regard to the composition of the EPDM rubber it is reasonable to suppose that the ethylene units, compared with those of propylene and diene, contribute to the second moment M_2 of the NMR spectra by the greatest proportion. For this reason we believe that the slower change of the second moment in the temperature range 160–220 K results from the oscillations of the chain segments in a way that was similar to that observed on the polyethylene samples.¹⁵

The *i*-PP/EPDM blend exhibits two steps of the second moment decrease in the temperature dependency of the second moment M_2 . They differ in their slopes and are located in the glass-transition temperature regions of the EPDM rubber and *i*-PP. The first decrease is observed in the region of 230–260 K and a motional process in this temperature range seems to be managed by motions of the EPDM rubber chains. The temperature region of the second decrease, observed above 260 K, is about the same as that revealed

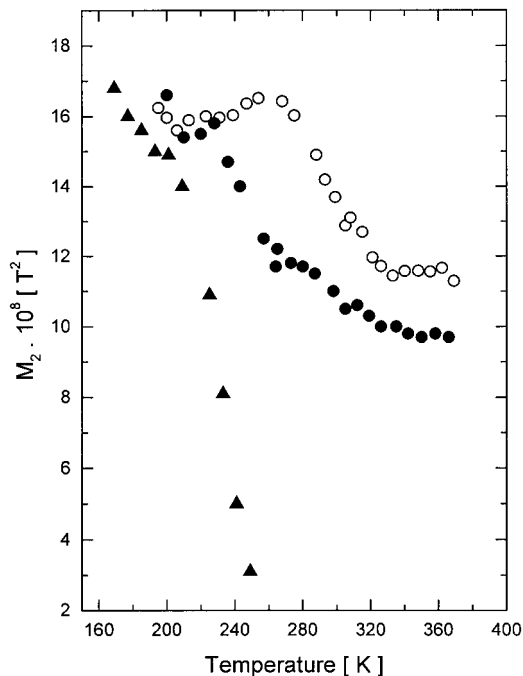


Figure 3 Temperature dependencies of the second moment M_2 of the spectra measured on the *i*-PP (○), EPDM rubber (▲), and *i*-PP/EPDM blend (●). The values of the second moment were determined within the experimental error of 5–10%.

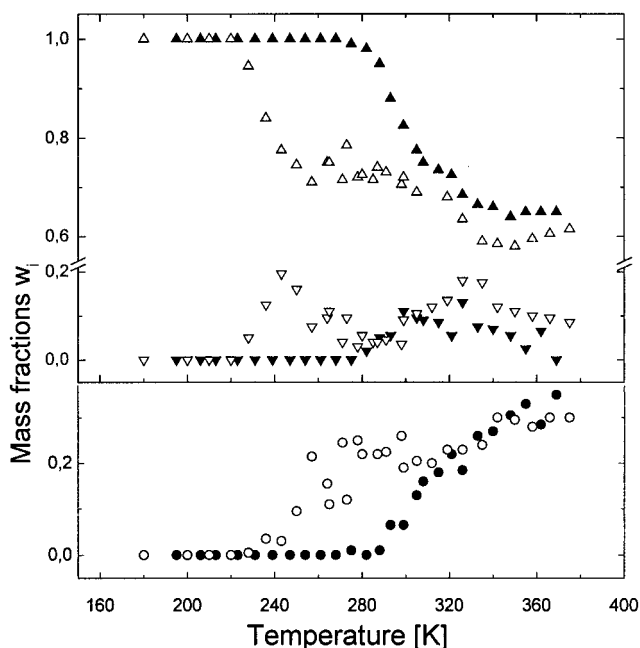


Figure 4 Temperature dependencies of the mass fractions w_n (●, ○), w_m (▼, ▽), and w_b (▲, △) related to the samples of the *i*-PP (solid symbols) and *i*-PP/EPDM blend (open symbols).

on *i*-PP. Then, the chain motion in the noncrystalline domains of *i*-PP could be responsible for the motional process in this temperature range.

The molecular motion related to the glass transition can be studied from the temperature dependencies of the parameters β_i and mass fractions w_i . The β_n^L determines the width of the narrow spectrum y_n and depends on the mobility of the chains within amorphous domains. The width δ_{nr} established as the difference between the magnetic fields corresponding to the maximum and minimum of the first derivative of the Lorentzian absorption spectrum, is given by the relation $\delta_n = 2\beta_n^L/\sqrt{3}$. The parameters of the middle component y_m , β_m^L and β_m^G that are related to the chains performing the hindered motion, determine its width and shape. With some oversimplification and in spite of the loss of some details of the analysis, we will interpret the temperature dependency of the width δ_m of the computed middle component y_m instead of the temperature dependencies of the two parameters β_m^L and β_m^G . The parameter S describes the width of the broad component with respect to the width of the low-temperature spectrum. It has been determined that its value slightly decreases with increasing temperature because of the expansion of the crystal lattice. The temperature dependency of that parameter is of no substantial importance in discussion on glass-transition phenomena.

The fractions w_i in fact determine the proportions of the number of the hydrogen protons related to the

chains with different mobility. They are identical with the mass fractions only in the case of the homopolymers, and generally this identity does not apply to copolymers and blends. However, because the proportions of the hydrogen protons differ very slightly from the mass fractions of the *i*-PP/EPDM blend, it is not necessary to distinguish between the mass fractions and proton fractions in this study.

Given that all chains of both the crystalline and noncrystalline regions are considered to be rigid below the glass-transition temperature T_g , the mass fraction $w_b = 1$ in this temperature range. A decrease of this value to 0.65 is observed in the temperature range 275–325 K in the case of *i*-PP (Fig. 4). It is reasonable to suppose that the molecular motion is activated within all noncrystalline domains at temperatures far above T_g and to consider w_b as the crystallinity of the *i*-PP sample. A small remainder of the rigid chains in noncrystalline regions follows from the difference between the observed value $w_b = 0.65$ at the temperatures 350–370 K and the crystallinity determined by means of the density. The increases of the mass fractions w_m and w_n were observed simultaneously with the decrease of mass fraction w_b .

The mobility of the noncrystalline chains performing free micro-Brownian and hindered motions as a function of temperature can be estimated from the temperature dependencies of δ_n and δ_{mr} respectively, shown in Figure 5. Both the narrow and middle com-

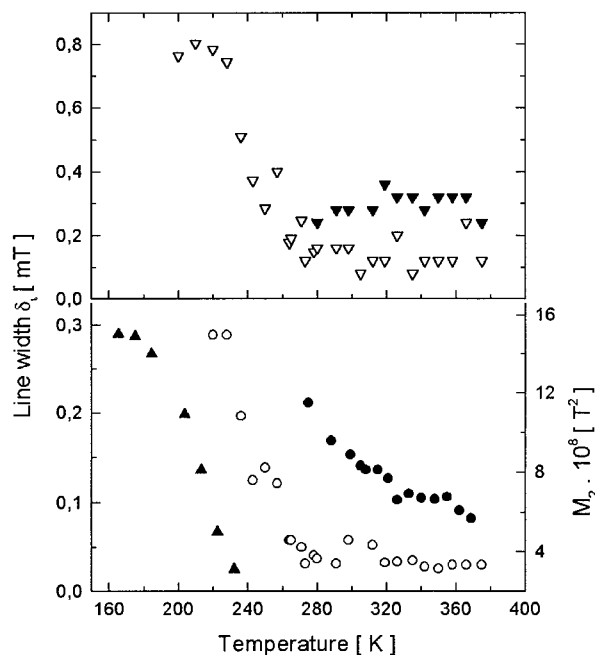


Figure 5 Temperature dependencies of the line widths δ_n (●, ○) and δ_m (▼, ▽) related to the samples of the *i*-PP (solid symbols) and *i*-PP/EPDM blend (open symbols) and of the second moment M_2 of the spectra measured on the EPDM rubber (▲).

ponents of the spectra measured on the *i*-PP appear at 270 K. The width δ_n of the narrow line decreases from 0.21 to 0.11 mT in the temperature range of 275–325 K and then, above this range, δ_n seems to be constant. On the other hand, the mass fraction changes there. Above 325 K, the mass fraction w_b is constant and the mass fraction w_n continues to increase at the expense of the small decrease of w_m . The width δ_m of the middle component y_m , related to the hindered motion of the noncrystalline chains, remains about 0.3 mT within the whole temperature range being discussed. Therefore, the variation of the temperature gives rise to the change of the amount of chains under consideration with corresponding change of their mobility.

Taking into account the dependencies of the mass fractions and the line widths depicted in Figures 4 and 5 it can be stated that the molecular motions in the noncrystalline regions of the *i*-PP/EPDM blend are excited at considerably lower temperatures than are those in the noncrystalline regions of *i*-PP. A decrease of w_b is observed in two steps, the first of which is located at 220–260 K, and then the plateau can be seen above 260 K. The rise of the temperature in the mentioned temperature range results in the activation of motion of the chains, the amount and mobility of which are determined by the mass fraction w_m and line width δ_m , respectively. The decrease of the line width δ_m from 0.8 to 0.18 mT in the range 210–270 K shows a mobility enhancement of the chains, the amount of which is seen to increase first, and then, above 240 K, the decrease of the mass fraction w_m can be observed in Figure 4. The spectrum y_m , which is usually related to the hindered chain motion in the intermediate regions, appeared at lower temperatures than the temperature at which the spectrum y_n was observed. We believe that the spectrum y_m observed in the temperature range up to 240 K is related to the amorphous chains with relatively low mobility. Afterward, above 240 K, because of a transformation of hindered motion into free motion that is seen from the increase of the w_n at the expense of w_m , the narrow spectrum y_n can be attributed to the amorphous chains.

The temperature dependency of the width δ_n for the *i*-PP/EPDM blend is considerably different from that for the neat *i*-PP. The motional process starts at 220 K, which is essentially lower, and the decrease of δ_n from 0.28 to 0.04 mT between temperatures 230–270 K is steeper than are those determined on the *i*-PP. To compare the glass-transition motional process in the *i*-PP/EPDM blend with that of the EPDM rubber the temperature dependency of the second moment M_2 of the spectra measured on the latter sample is also depicted in Figure 5. The mass fraction w_n in the blend increases in the temperature range 230–270 K up to 0.25 and at temperatures above 300 K takes up the same values as those for the *i*-PP.

The temperature dependency of the mass fractions w_b for the *i*-PP/EPDM blend exhibits the second decrease in the region of 320–330 K, and then the high-temperature plateau is seen above this temperature range. The behavior of each of the mass fractions, w_n , w_m , and w_b , at temperatures above 320 K is very similar to that calculated for *i*-PP. It is obvious from the data that crystallinity of the blend is lower and, on the other hand, the amount of the intermediate chains is higher compared with those for the neat *i*-PP. Both the δ_n and δ_m seem to be decreasing only very slightly above 270 K; thus neither the decrease of the line width δ_n nor that of δ_m is observed in the temperature range above 260 K where the second moment decreases (see Fig. 3). The values of δ_n and δ_m are substantially lower compared with that found for the *i*-PP within the broad temperature range.

Analysis of the experimental results described above enables us to draw conclusions regarding the nature of the motional processes related to the glass transition of the *i*-PP/EPDM blend. Two decreases in the second moment M_2 temperature dependency reveal the double glass transition. The lower glass transition is located between the glass transitions of EPDM rubber and that of *i*-PP but nearer to the glass transition of the former. The increases of the mass fractions w_n and w_m in the lower glass-transition temperature region show the gradual activation of the motion within noncrystalline regions and the decreases of the line widths of the δ_n and δ_m reveal the enhancement of chain mobility. The discussed glass-transition motional process detected by the temperature dependencies δ_n and δ_m , compared to the glass-transition motional process of the EPDM rubber detected by the temperature dependency of the second moment M_2 , is shifted toward the higher temperatures. Consequently, the lower glass transition of the *i*-PP/EPDM blend arises from the polymer regions with blended *i*-PP and EPDM rubber chains rather than from the neat EPDM rubber domains.

The upper glass transition is located in the glass-transition temperature region of the neat *i*-PP and the motional process differs from that connected to the lower transition. In the case of the upper glass-transition motional process, the second moment cannot be related to the change of the line width of either of the components. The transformation of the rigid chains into the hindered mobile chains, which follows from the mass fractions w_b and w_n , elucidates the second moment behavior. The dependencies of the mass fractions w_n and w_m show the transformation of the hindered motion into free motion above 320 K. The interpenetration of the EPDM rubber and *i*-PP chains in both the amorphous and intermediate regions of the *i*-PP/EPDM blend can be deduced from the higher amount of the intermediate chains in the *i*-PP/EPDM blend compared to that in the *i*-PP and from the per-

centage of the EPDM rubber in the blend. The smaller widths of narrow and intermediate lines for the blend compared to those for neat *i*-PP (Fig. 5) also corroborate an interpenetration of the EPDM chains into the intermediate and amorphous regions of neat *i*-PP.

Within the broad temperature range, which is above the lower glass transition of the *i*-PP/EPDM blend, the line widths of the narrow component δ_n and of the middle component δ_m that are related to amorphous and intermediate regions of the *i*-PP/EPDM blend, respectively, are several times lower than are those related to the corresponding regions of the *i*-PP. Therefore, the mobility of the chains of the noncrystalline region of the *i*-PP/EPDM blend is considerably higher than that in the noncrystalline regions of the neat *i*-PP.

Recently, *i*-PP/EPDM blends with different proportions of components were studied by means of dynamic mechanical thermal analysis, transmission electron microscopy, and differential scanning calorimetry.¹⁶ The two glass-transition temperatures, a certain degree of miscibility, and the slightly lower crystallinity of the *i*-PP/EPDM blend compared with those of the neat *i*-PP are features that were also confirmed in our analysis of the broad-line ¹H-NMR spectra.

CONCLUSIONS

The double glass transition was found in the *i*-PP/EPDM blend by means of the broad-line ¹H-NMR measurements performed within the broad temperature range. The gradual increase in the number of chains and enhancement of the chain mobility within noncrystalline regions, both as a function of the temperature, are responsible for the motional process related to the lower glass transition observed in the temperature range 220–260 K. A different mechanism elucidates the relaxation related to the upper glass transition at 300–330 K. The mobilities of the noncrystalline chains performing either hindered or free micro-Brownian motion vary very slightly with the tem-

perature and the relaxation is realized by the transformation of the hindered motion into free motion.

Interpenetration of the EPDM rubber and *i*-PP chains within both the amorphous and intermediate domains of the *i*-PP/EPDM blend was inferred from the data. The *i*-PP/EPDM blend compared to the neat *i*-PP contains the same amount of amorphous chains and a higher amount of the intermediate chains. Consequently, the crystallinity of the *i*-PP/EPDM blend is lower than that of the *i*-PP.

The mobilities of the amorphous and intermediate chains of the *i*-PP/EPDM blend were deduced to be considerably higher than the mobilities of the amorphous and intermediate chains of the *i*-PP, respectively.

This work was supported by the Slovak Grant Agency (project 1/7402/20) and partly supported by the Grant Agency of the Czech Republic (project 106/02/1249) and Grant Agency of the Academy of Sciences of the Czech Republic (project KSK4050111).

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