

BROAD LINE NMR STUDY OF MODIFIED POLYPROPYLENE FIBRES**D. Olčák, L. Ševčovič, L. Mucha***Department of Physics, Technical University, 041 20 Košice, Slovakia*

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Study of drawn fibres prepared from an isotactic polypropylene modified by an ethylene aminoacrylate copolymer has been done using the broad line of ^1H NMR. NMR spectra were measured on the set of fibres prepared with a draw ratio λ from 1 to 5.5 at two temperatures, one of them corresponding to the onset of segmental motion and the other one is the middle of the temperature interval as determined by decrease of the second moment M_2 . Decomposition of the spectra into elementary components related to the amorphous, intermediate and crystalline regions of partially crystalline polymers has been made. The drawing of the fibres was found to enhance the chain mobility in the amorphous region and to restrain the molecular motion in the intermediate region. Such behaviour well supports conclusions predicted in the earlier study based on the spin-lattice relaxation time T_1 and dynamic mechanical data treated using the WLF theory.

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1 Introduction

The previous study of relaxation process in drawn fibres prepared from the modified isotactic polypropylene (PP) has shown differences in studies using different dynamic methods. Influence of drawing on the relaxation processes connected with the glass transition (β process) in the PP fibres has been studied in terms of the spin-lattice relaxation times T_1 and storage (E') and loss (E'') components of the dynamic modulus. It was found that drawing of the modified PP fibres gives rise to the shift of the minimum of the temperature dependence of the spin-lattice relaxation times T_1 measured at the resonant frequency 30 MHz towards higher temperatures. On the other hand, the maximum of the loss modulus detected at the operating frequency 110 Hz was shifted to the lower temperatures. Two different molecular mechanism were assumed for an explanation of this contradictory behaviour [1].

In partially crystalline polymers, the rise of crystallinity, which e.g. can arise from drawing, results usually in the shift of T_g to the higher temperatures [2]. In contrast to the conventional behaviour, our previous calculations of T_g , which were carried out by the WLF equation [3], used the data corresponding to the positions of extremes of the above mentioned temperature dependencies, have predicted an opposite effect. In spite of the rise of crystallinity in consequence of drawing, the decrease of the glass transition temperature T_g was found out. The aim of this

Fig. 1. The dependence of density ρ (\circ) and crystallinity X_c (\bullet) on the draw ratio λ of the PP-8/400/ λ fibres.

paper is to specify reasons of the previously predicted phenomena and to find how the particular molecular mechanisms are related to the multi-phase structure of the studied fibres. It is well known that broad line NMR spectra are sensitive to the chain mobility, which consequently depends on the morphology of the polymer. Therefore, in order to reach our intention, the broad line ^1H NMR experiments were performed on the set of the PP fibres with the different draw ratio λ at properly chosen temperatures.

2 Experimental

The fibres were prepared from the commercial polypropylene Mosten D3, which was melted with an ethylene aminoalkylacrylate copolymer. PP modified in this way contained 8 wt% of the copolymer. Spinning was performed at 270°C at a speed of 400 m/min. Samples were drawn at 130°C at various draw ratio λ using laboratory apparatus. The fibres with the draw ratio λ from 1 to 5.5 were prepared for our study. They were denoted as PP-8/400/ λ according to the quantity of modifier, spinning speed and the draw ratio. Crystallinity X_c of the fibres was estimated from the X-ray dispersion curves as a ratio of the area corresponding to the crystalline dispersion peak to that corresponding to the whole dispersion. Both the crystallinity X_c and the density ρ which was determined by the floating technique, are depicted in Fig. 1. as functions of the draw ratio λ . Measurements of the both quantities were performed at the Research Institute of Man-Made Fibres in Svit (Slovakia). The other characteristics of the investigated materials can one found in [1].

The broad line ^1H NMR spectra were measured on the samples prepared from fibres densely wound on a thin teflon rod and then inserted into the glass tube of diameter of 10 mm. The measurements were carried out using spectrometer constructed in our laboratory [4]. The spectrometer operates at fixed magnetic field $B_0 = 0.247\text{ T}$ ($f_0 = 10.5\text{ MHz}$) using frequency sweep. The sweep range was 5 mT and 1024 channels NMR spectra has been used. All spectra were detected at the temperatures 265 K and 313 K using the same operating parameters. In order not to

Fig. 2. The derivations of the broad line NMR absorption detected on the PP-8/400/ λ fibres with the draw ratios $\lambda = 1$ (●) and 5.0 (○) at 265 K. Due to the symmetrical shape of all spectra only their halves are depicted in this figure.

Fig. 3. The second moment M_2 of the NMR spectra measured at 265 K (●) and 313 K (○) as a function of the draw ratio λ .

influence the shape of the spectra, the operating parameters of the spectrometer were minimized. The frequency sweep, amplitude of the modulating field B_{mod} and the time constant of lock-in amplifier were $0.46 \mu\text{T s}^{-1}$, $22 \mu\text{T}$ and 0.1 s, respectively. The frequency of the modulating field was 40 Hz. To improve signal to noise ratio, at least six scans were accumulated.

3 Results and discussion

The temperature dependences of the second moment M_2 of the spectra measured on the isotactic polypropylene at temperatures above 77 K first show a plateau related to both the CH_3

Fig. 4. The derivation of the broad line NMR absorptions detected on the PP-8/400/ λ fibres with the draw ratios $\lambda = 1$ (●) and 5.0 (○) at 313 K.

group rotation and rigid main chains. At higher temperatures the step-like decrease of the second moment, which is connected to the segmental motion is observed above T_g . The chosen temperatures 265 K and 313 K are related to the onset of the segmental motion and to the middle of the temperature range of the second moment decrease, respectively.

The glass transition temperatures T_g of 262.8 K ($\lambda = 1$), 255.7 K ($\lambda = 2.5$), 252.3 K ($\lambda = 3.5$) and 264.4 K ($\lambda = 5$) corresponding to fibres PP-8/400/ λ with the different draw ratio λ were calculated in [1]. The NMR spectra measured at the temperature 265 K which is slightly above the T_g of undrawn ($\lambda = 1$) fibres provide an experimental evidence of the predicted T_g behaviour. The spectra of all samples with the exception of the undrawn fibres have a small narrow peak, which can be seen in Fig. 2. in the spectrum of the PP-8/400/5 fibres. This means that the molecular motion related to the glass transition in the drawn fibres appears at lower temperatures than that in the undrawn ones. Fig. 3. shows that an appearance of the narrow peak in the spectra of drawn PP fibres does not give rise to the change of the second moment M_2 at 265 K.

Unlike the second moment M_2 of the spectra measured at 265 K, the second moment detected at 313 K, which is sufficiently far above the glass transition T_g , shows an increase in the dependence of the M_2 vs. the draw ratio λ (Fig. 3). This increase may be explained by the transformation of the intermediate (constrained amorphous) chains into the crystalline phase and by the restriction of the motion in the noncrystalline regions in consequence of drawing. The former assumption, which also may be understood as restriction of the chain mobility, can be confirmed by the increase of the crystallinity vs. the draw ratio λ (Fig. 1).

The change of the chain mobility arising from drawing can be immediately deduced from the spectra of the undrawn and drawn PP fibres measured at 313 K. Fig. 4. shows that drawing results in the considerable narrowing of the peak in the spectrum.

It is well known that the broad line NMR spectra can be decomposed into several components corresponding to the different kinds of molecular motions realized in different morphological regions of the polymer. A three-phase structural model of partially crystalline polymers with crystalline, intermediate and amorphous regions, which is frequently used to interpret the NMR

Fig. 5. The decomposition of the broad line NMR spectrum measured on the undrawn PP-8/400/1 fibres at 313 K. The calculated spectrum y_c consists of the narrow y_n , middle y_m and broad y_b elementary spectra weighted by the corresponding relative mass fractions w_i ($i = n, m, b$).

Fig. 6. The relative mass fractions w_i ($i = n, m, b$) corresponding to the narrow (\bullet), middle (\square), and broad (∇) elementary spectra as functions of the draw ratio λ .

data, can be represented by that presented by Struik. The main feature of this model is that the crystalline regions disturb the amorphous phase and reduce its segmental mobility. This reduction is the most expressive in the immediate vicinity of crystallites. At large distances from the crystallites, the properties of the non-crystalline phase become equal to those of the bulk amorphous material [5]. In the case of fibres in the oriented state, taut tie molecules between subsequent crystal blocks of a microfibril and taut tie molecules connecting microfibrils also form the intermediate phase with reduced chain mobility.

A technique of the analysis suggested by Bergmann and verified by several authors enables to decompose the NMR spectrum into three elementary spectra y_n (narrow), y_m (middle) and y_b

Fig. 7. The parameters of the narrow β^L (\bullet), middle β_m^L (Δ), β_m^G (\circ), δ_m (\square) and broad S (∇) elementary spectra, respectively, as functions the draw ratio λ . β^L is the parameter of the Lorentzian function, β_m^L and β_m^G are parameters of the product of the Lorentzian and Gaussian functions, δ_m is the width of the middle elementary spectrum and S is the scaling factor, which is related to the width of the broad elementary spectrum.

(broad) ones related to the amorphous (micro-Brownian motion), intermediate (hindered motion) and crystalline (rigid chains) regions, respectively [6,7]. Usually, the narrow component y_n is the Lorentzian function, the middle one y_m is the product of Gaussian and Lorentzian function and the broad elementary spectrum y_b is derived from the measured low temperature spectrum. The spectrum y_c calculated in terms of the elementary spectra y_n , y_m and y_b can be expressed by the equation

$$y_c = w_n y_n(x, \beta^L, \beta_{\text{mod}}) + w_m y_m(x, \beta_m^L, \beta_m^G) + w_b y_b(x, S) \quad (1)$$

in which $x = B - B_0$ is a difference between the applied magnetic field induction B and the resonance magnetic field B_0 . The relative mass fraction w_i ($i = n, m, b$) and parameters of the elementary spectra β_i and S were obtained by the least square method. Influence of the modulation field on the narrow elementary spectrum y_n was considered in our computations. Other details of the analysis can be found in [8].

We have found out that the low temperature spectra measured at 200 K on the samples PP-8/400/ λ do not show any differences, therefore all the spectra measured at 313 K could be treated by the same low temperature spectrum. The analysis described above is illustrated in Fig. 5. on the sample PP-8/400/1. The mass fractions w_n , w_m and w_b and the parameters corresponding to the narrow (β^L), middle (β_m^L and β_m^G) and broad (S) elementary spectrum are depicted in Figs. 6 and 7, as dependences on the draw ratio λ .

The mass fractions w_i estimated from the spectrum at a given temperature determine the fractions of the chains undergoing the micro-Brownian motion (w_n), hindered motion (w_m) and of the rigid chains (w_b). An enhancement of the rigid fraction and the decrease of both the fractions of the chains undergoing the micro-Brownian motion and of the hindered chain motion in consequence of drawing can be deduced from Fig. 6. We suppose that the transformations

of the amorphous chains into intermediate and intermediate chains into crystalline are the most probable mechanism which can explain dependences w_i vs. λ .

The influence of drawing on the molecular motion in individual phases of the polymer can be drawn from the parameters of the individual elementary spectra (Fig. 7). The decrease of β^L shows the chain mobility enhancement in the amorphous regions of the PP owing to the drawing. The parameters β_m^L and β_m^G determine the width and shape of the middle component and they depend on the chain mobility in the intermediate regions. In our qualitative discussion we will use the width of the middle component δ_m , which was established as the difference between magnetic fields corresponding to the maximum and minimum of the computed middle component or as double of x corresponding to the maximum of the middle line y_m , instead of the two parameters β_m^L and β_m^G (Fig. 5). It can be noted that the course of δ_m follows that of β_m^L in Fig. 7. The increase of the width δ_m as a function of the draw ratio λ reveals the restriction of the molecular motion in the intermediate regions. It can be drawn from this figure that the drawing causes no change of the width of the broad elementary spectrum y_m which is represented by the scaling factor S .

As we mentioned above, the NMR spectra measured at 265 K show that the narrow peak in the spectrum of the drawn fibres appears at the lower temperature than that of the undrawn. This fact together with the discussed narrowing of the narrow component, observed at 313 K, enable us to conclude that the higher is the draw ratio λ the shorter are the correlation times τ_c of the segmental motion at the given temperature. The chain mobility enhancement was previously predicted [1] from the free volume increase which was deduced from both the density, which is independent on the draw ratio λ and the rise of the crystallinity as a function of λ (Fig. 1). The conclusion made above shows agreement with our earlier calculations [1] only over the temperature range from T_g to 320 K. But, as we mentioned above, the drawing leads also to the restriction of the molecular motion in the intermediate regions and thereby to increase of the correlation times τ_c . It is reasonable to suppose that this motion is excited at higher temperatures than that in amorphous regions. We believe that chain mobility restriction discussed above is the same phenomenon as that which was observed by the shift of the temperature dependences of the spin-lattice relaxation times T_1 to the higher temperatures [1,9,10]. This restriction was ascribed to the increase of macromolecular order in the noncrystalline regions [10].

Therefore, there are contradictory molecular processes in the noncrystalline regions of the modified PP fibres. If the mentioned restriction of the molecular motion in the intermediate regions dominates above loosing of the chain mobility in the amorphous regions higher values of the average correlation times τ_c may be observed in the drawn modified PP fibres. This is the case which was predicted from our calculations for the temperature range above 320 K up to $T_g + 100$ K.

4 Conclusions

We have found out that the drawing of the modified PP-8/400/ λ fibres results in the increase of the chain mobility in the amorphous regions and, therefore, to the decrease of the correlation times τ_c of the molecular motion in these regions. The restraint of the chain mobility in the intermediate regions and thereby the increase of the correlation times τ_c were also found.

The molecular processes revealed in the amorphous and intermediate regions of the studied

fibres provide an explanation of the temperature dependence of the average correlation times τ_c and of the unconventional effect of the drawing on the glass transition temperature T_g behaviour, which were predicted from the spin-lattice relaxation times T_1 and dynamic mechanical data with the use of the WLF theory in our previous study.

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