Study of β Relaxation in Polypropylene Fibres Modified by Several Techniques

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Summary: Polypropylene fibres prepared from polypropylene (PP) blended with 8 wt % of an ethylene aminoalkylacrylate copolymer were studied by means of ^{1}H nuclear magnetic resonance (NMR) and dynamic mechanical techniques. Measurements were carried out on the fibres spun at the spinning speeds 400 and 1200 m.min^{-1} and then drawn to the draw ratio λ = 3.5. Spin – lattice relaxation time T_1 and storage E' and loss E'' components of a dynamic mechanical modulus were measured in the temperature region of the glass transition. Broad line NMR spectra were detected at 313 K. The experimental results show that drawing of the fibres prepared at both spinning speeds results in a restriction of the molecular motion. Simultaneously with the restriction, a chain mobility enhancement was observed in noncrystalline regions of the fibres. Similar effects were induced also by rising the spinning speed. Reasons for this behavior are discussed in the paper.

Introduction

Glass transition phenomena in partially crystalline polymers strongly depend on the supramolecular structure, which can be modified by different physical and chemical techniques. In the past, several papers studied an influence of drawing of PP fibres and films on chain mobility related to the glass transition. Drawing usually results in an increase of macromolecular arrangement and consequently in molecular motion restriction in noncrystalline regions$^{1)}$. On the other hand, a decrease of activation energy of the chain motion related to the glass transition as a function of draw ratio λ was observed for PP fibres with different properties$^{2,3)}$. Obviously, if only the restriction of the molecular motion as a result of the higher macromolecular arrangement occurred then an increase rather than a decrease of the activation energy should be observed.

Isotactic PP exhibits the helical molecular chain conformation as the most stable one, whereas the planar zig-zag form is more energetically favorable structure for a number of linear crystalline polymers. The helical molecular chain conformation of PP is typical for crystalline domains but it was shown with the use of the ^{13}C NMR that this

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conformation is held to some extent even in a crystalline-amorphous interphase[4)]. The helical arrangement of PP chains is kept due to methyl side groups giving the energy barriers, which hinder transformation to the straightened zig-zag conformation.

A resembling effect as that brought about by the drawing was observed in an application of a tensile load to the PP fibres. It was found that a reversible elastic deformation of PP helices under external forces also results in an enhancement of chain mobility. A deformation of helices resulting from the action of external forces produces an increase of the distances between methyl group centers and, in this way, a decrease of the energy barriers. Then, a number of possible conformations may be achieved which consequently stimulate the micro-Brownian motion. From a number of the investigated polymers only the PP fibres have shown such unusual properties[5)].

Recently, two papers dealing with the study of the molecular motion related to the glass transition phenomena in the drawn PP fibres were published[3,6)]. Two contrary relaxation processes induced by drawing were found by means of the spin – lattice relaxation time T_1 and dynamic mechanical measurements. The analysis of the experimental data showed that drawing results in restraints of the molecular motion arising from a higher arrangement of macromolecular chains and simultaneously in the shift of the glass temperature T_g to lower temperatures, which reflects the enhancement of the molecular motion. It follows from the broad line NMR spectra that the chain mobility enhancement is related to the amorphous regions and the restraints of the chain mobility to the intermediate regions. The activation energy which, according to the Williams – Landel – Ferry theory, depends on the temperature, was found to decrease with increased draw ratio at a given temperature. The free volume increase was accepted as a reason of both the chain mobility enhancement and the activation energy decrease.

The fibres spun at the spinning rate 400 m/min and then drawn to the different draw ratios were used in our previous studies[3,6)]. However, the crystallization proceeds during cooling of the polymer flow under the action of deformation forces. The axial strength induced by spinning apparatus influences a chain arrangement into higher morphological structures. The fibres prepared at a low spinning rate exhibit the spherolitical structure with a low degree of orientation and, on the other hand, a system of anisotropic fibres is obtained at a higher spinning rate. If the rate is sufficiently high the fibres possess the fibrillar structure[7)]. It is reasonable to expect also an influence of spinning speed on the chain arrangement and the chain mobility. That is why this study of drawn PP fibres modified by the polymer additive and spun at different spinning speeds was done by using NMR and dynamic mechanical techniques.

Experimental

The measurements were made on fibres prepared from the commercial polypropylene Mosten D3[8)], which was melted with an ethylene aminoalkylacrylate copolymer. PP modified in this way contained 8 wt-% of the copolymer. The fibres were denoted as PP-8/400/λ or PP-8/1200/λ according to the quantity of the copolymer, spinning speed (400 or 1200 m/min) and draw ratio λ.

The broad line ^{1}H NMR spectra were measured on the spectrometer, which operates at the fixed magnetic field $B_0 = 0.247$ T, using frequency sweep at 313 K. The frequency was swept with the step of 208 Hz carried out after time of 11 s. The amplitude of modulating field B_{mod} and the time constant of the lock-in amplifier were 22 μT and 0.1 s, respectively.

The spin – lattice relaxation times T_1 were measured using the 90°_{sat} - τ - 90 pulse sequences at the resonant frequency $f_0 = 30$ MHz over the temperature range from 290 to 430 K.

The dynamic mechanical measurements were performed on the Rheovibron, model DDV-II-C at the frequency $f_E = 110$ Hz in the temperature range 220 – 370 K.

Other data concerning samples and conditions of measurements can be found in the papers[3,6)].

Results and Discussion

The spin – lattice relaxation time T_1 and dynamic mechanical measurements enable to detect molecular motions with correlation times τ_c of about 10^{-9} s (T_1) and 10^{-3} s (E") under chosen conditions of experiments. Temperature dependencies of the spin – lattice relaxation times T_1 depicted in Fig. 1 show that both the drawing and the increase of the spinning speed result in similar effects. They shift minimum to higher temperatures and give rise to the increase of the spin – lattice relaxation time $T_{1,\ min}$ related to the minimum (Tab. 1). The former effect reflects restriction in the chain mobility, which in both cases can be related to the increase of macromolecular orientation seen from the birefringence Δn introduced in Tab. 1. Spin diffusion phenomena and the rise of crystallinity X_c (Tab. 1) relate to the increased $T_{1,\ min}$ values[1)]. It can be noted that drawing of the fibers spun at the higher rate results in a substantially higher temperature shift of the T_1 minimum than in case of the fibres prepared at the lower rate.

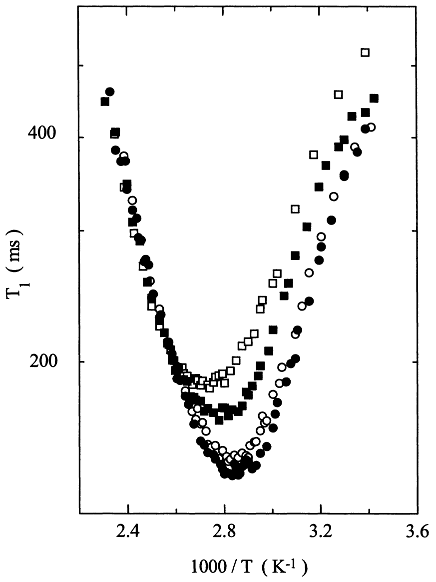

Fig. 1. Temperature dependencies of the spin-lattice relaxation time T_1 measured on the undrawn PP-8/400/1(●) and PP-8/1200/1 (o) fibres and on the drawn PP-8/400/3.5 (■) and PP-8/1200/3.5 (□) fibres.

Table 1. λ - draw ratio, X_c – crystallinity, Δn – optical birefringence, ρ - density, T_{min}, $T_{1,min}$ – coordinates of the minimum of the temperature dependence of the spin-lattice relaxation times T_1.

	λ	X_c (%)	Δn x 10^3	ρ (kg m^{-3})	$T_{1,min}$ (ms)	T_{min} (K)
PP8/400/λ	1.0	49	2.3	899	141	352
	3.5	59	25.8	898	168	361
PP-8/1200/λ	1.0	55	13.5	897	149	353
	3.5	67	29.4	901	187	370

Behavior of the dynamic mechanical data does not completely coincide with the spin lattice relaxation times T_1. Both, the drawing and the increase of the spinning speed cause the rise of the storage modulus E' measured in the whole temperature range (Fig.2). In the case of drawing, this tendency can be explained by the increase of both the number and tightness of the tight chains$^{9)}$ that supports the chain mobility constraints. The temperature dependencies of E' show that also increase in the spinning speed induces a hardening effect. On the other hand, the shift of the maximum of the temperature dependencies of loss modulus E'' to the lower temperatures was caused by drawing$^{3)}$ and similar effect was observed for the undrawn fibres prepared at higher spinning speed (Fig. 2, Tab. 2). Therefore, a loosening of the molecular motion instead of its restriction is detected from the loss modulus data E''.

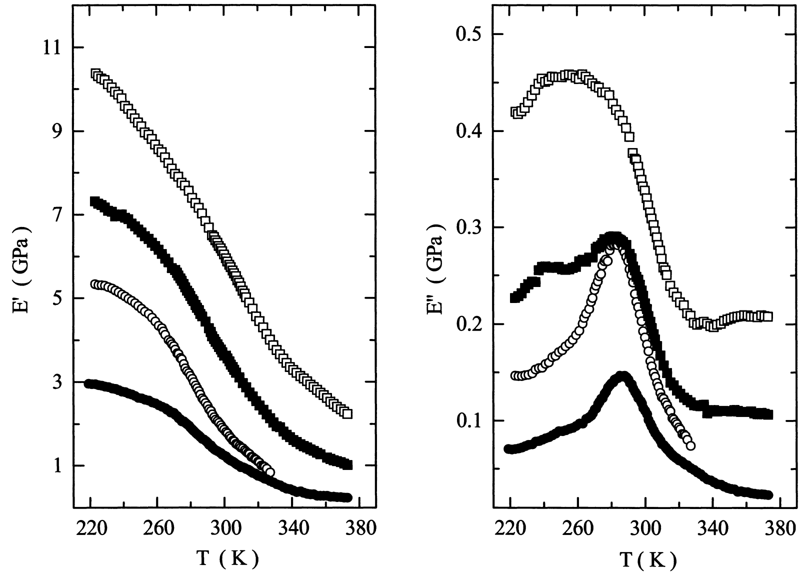

Fig. 2. Temperature dependencies of the storage E' and loss E" moduli measured on the undrawn PP-8/400/1(●) and PP-8/1200/1 (o) fibres and on the drawn PP-8/400/3.5 (■) and PP-8/1200/3.5 (□) fibres.

The minima and maxima of the temperature dependencies of the spin - lattice relaxation times T_1 and loss modulus E'', respectively, are situated in the temperature range from T_g to T_g + 100 K. For this temperature range the Williams – Landel – Ferry equation can be used for interpretation of the experimental results. Using Eqs. (8) and (9) in the paper[3)], the glass transition temperature T_g and isothermal activation energy E_a were evaluated from the measured data. The calculations show that drawing decreases the glass transition temperature. The temperature corresponding to the maximum of the loss modulus for the drawn fibres spun at higher speed cannot be determined because the peaks are broad and overlapped with the lower temperature γ relaxation peak. Therefore, the glass transition temperature T_g and activation energy E_a can be determined only for the undrawn fibres. Data in Tab. 2 reveal that both quantities decrease by increasing the spinning speed.

Table 2. T_{max}, $E“_{max}$ - coordinates of the maximum of the temperature dependencies of the loss modulus E“, T_g - glass transition temperature, $E_{a,300}$ -activation energy at 300 K.

	λ	$E“_{max}$ (Gpa)	T_{max} (K)	T_g (K)	$E_{a,300}$ (kJ mol^{-1})
PP8/400/λ	1.0	0.145	286	263	197
	3.5	0.290	280	252	159
PP-8/1200/λ	1.0	0.283	283	258	176

The broad line NMR spectra were decomposed into three elementary components related to the amorphous (with the chains performing micro-Brownian motion), intermediate (hindered motion) and crystalline (rigid chains) regions (Fig. 3), which are characterized by the relative mass fractions and by the width parameters[6)]. A comparison of the parameters in Tab. 3 leads to the conclusion that drawing of the fibres prepared at both spinning speeds has an equal effect. The decrease of the mass fractions corresponding to the amorphous (w_n) and intermediate (w_m) regions, the narrowing of the elementary spectrum related to the amorphous regions and the broadening of that related to the intermediate region can be observed. But it can be seen from the data corresponding to the same draw ratios in Tab. 3 that the increase of the spinning speed gives rise to some different effects. The decrease of the width of the narrow component is the only common effect caused by both the rise of the spinning speed and the drawing, and it can be classified as a chain mobility enhancement in amorphous regions. The various spinning speeds, unlike drawing, do not result in the substantial differences between corresponding mass fractions.

The increase of crystallinity both with the draw ratio and the rise of the spinning speed, without changing the density (Tab. 1), indicates the increase in the free volume. We assume that this phenomenon has an origin in enhancement of the chain mobility and in decrease of the activation energy. The reason for the free volume increase is unclear at the moment.

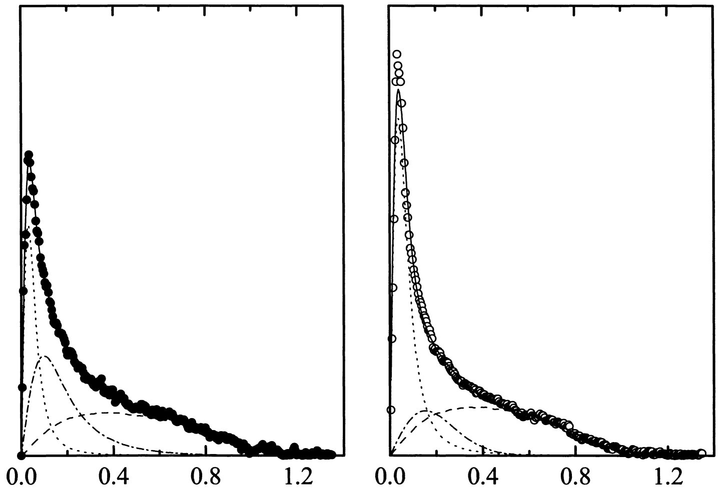

Fig. 3. Broad line NMR spectra for the undrawn PP-8/400/1(●) and PP-8/1200/1 (o) fibres. The spectra are decomposed to the narrow, middle and broad components related to amorphous (micro – Brownian motion), intermediate (hindered motion) and crystalline (rigid chains) regions, respectively.

Table 3. w_i (i = n, m, b) – relative mass fractions related to amorphous (micro – Brownian motion), intermediate (hindered motion) and crystalline (rigid chains) regions, β_L, δ_m, S – the width parameters related to the narrow, middle and broad elementary spectrum, respectively.

	λ	w_n	w_m	w_b	β_L (mT)	δ_m (mT)	S
PP8/400/λ	1.0	0.062	0.231	0.707	0.045	0.196	0.914
	3.5	0.037	0.179	0.784	0.038	0.216	0.945
PP-8/1200/λ	1.0	0.075	0.264	0.661	0.034	0.186	0.870
	3.5	0.036	0.141	0.823	0.028	0.225	0.920

The solid state ^{13}C NMR(4) provides the information that PP with crystalline and amorphous phases contains also the noncrystalline chains with the helical molecular conformation and with somewhat restricted molecular motions compared to the amorphous phase. In connection to the results of paper(5) it is reasonable to suppose that these chains consist also from the tight chains, which are the most strained. These chains are responsible for any deformation of the noncrystalline helices under drawing.
The mass fractions reveal the complex structural transformations occurring during drawing. A possible explanation is the transformation of the helices connecting crystalline blocks into zig-zag structure resulting in the extended length of the chains. In such way the larger distances between crystalline blocks can be achieved. The change of the chain mobility in amorphous regions due to increasing the spinning speed can be related to the deformation of the compact spherolitical structure in the course of spinning(7).

Conclusions

Regardless of the spinning speed, drawing of the investigated PP fibres results in the chain straightening and molecular motion restrains and also in the molecular motion enhancement. The observed effects were found to be more intense in the case of the fibres spun at the higher speed. The rise of the spinning speed leads to the qualitatively similar effects as drawing. An increase in the free volume, which was induced both by drawing and by increasing the spinning speed, gives an explanation for the enhancement in the chain mobility.

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