Evolution of physical and mechanical properties during phase transformation in poly(1-butene)

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Abstract: The work is focused on study of evolution of the physical and mechanical properties of poly(1-butene) (PB-1). This evolution was observed during the phase transformation from the metastable form II to the thermodynamically more stable form I. Three different commercially-available grades of PB-1 were used in this work; two homopolymers and one ethylene copolymer. Specimens were prepared by compression molding with three various thickness and by extrusion This specimens were annealed at five various temperatures of -22, 5, 22, 40, and 60 °C during a time. Content of the form I in specimens was calculated by wide angle X-ray scattering during the phase transformation. Physical properties were measured via density changes of specimens and changes of mechanical properties were measured via tensile testing. From density measurements, it is obvious that the different thicknesses of compression-molded specimens do not influence the evolution of rate of the phase transformation. Densities of compression-molded and extrudates posses virtually the same values after the phase transformation. The evolution of the Form 1 content was confirmed by the trends, which were observed, via density measurements and by tensile testing in the evolution of tensile modulus. The evolution of tensile properties was carried out on extrudates and the results were consequently compared with the evolution of injection-molded specimens. From this observation it was found that values of moduli in extrudates are remarkably higher than in the injection-molded specimens. This is a consequence of different morphological structures, which have direct impact on mechanical properties and the phase transformation in PB-1. It is evident that processing is a key parameter influencing mechanical properties and together with annealing temperature significantly influences the rate of the phase transformation of PB-1.

Key-Words: Poly(1-butene), phase transformation, physical properties, mechanical properties.

1 Introduction

Poly(1-butene) belongs to group polyolefins which are a large class of carbon-chain elastomeric and thermoplastic polymers usually prepared by addition (co)polymerization of olefins or alkenes such as ethylene. [1] PB-1, like polyethylene or polypropylene has a unique morphology and crystallization behavior combined with carefully controlled molecular parameters give PB-1 a profile of properties which combines typical features of conventional polyolefins and particular characteristics of technical polymers. PB-1 displays excellent resistance to creep, abrasion, chemicals and environmental stress cracking.

Natta et al. investigated the polymerization of 1-butene in the same period as their studies of polypropylene. They succeeded in producing isotactic polybutene-1 in 1954 and determined its crystal structure to prove its stereoregularity. It was characterized by peculiar polymorphic characteristics in which it would initially crystallize into first form (form II) and then, within hours, re-crystallize into a second form (form I). [2]

Poly(1-butene) exhibits five crystal modifications depending on the formation conditions: forms I, twined hexagonal with a 3/1 helix; I', II', untwined hexagonal with a 3/1 helix; II, tetragonal with an 11/3 helix; and III, orthorhombic with a 4/1 helix. [3] The most important phenomenon is the transformation of form I into form II, which takes place in PB-1at room temperature after crystallization from the melt. This crystalline structure crystallizing from the melt is known as form II. It is unstable and transforms into a more stable form I at room temperature and atmospheric pressure. This transformation results in the desirable properties of the material as previously discussed. [4]

The aim of this work was to describe evolution of physical and mechanical properties during phase transformation. To these purpose three grades of isotactic poly(1-butene) by Basell Polyolefins, Louvain la Neuve, Belgium were used. Specimens designed for observation of evolution of physical and mechanical properties were prepared via extrusion and compression molding. Accordingly to the aim, following experimental techniques were used: density measurement, wide angle X-ray scattering and tensile testing.

2 Experimental

2.1 Materials

In this study, three commercially-available grades of isotactic poly(1-butene) by Basell Polyolefins, Louvain la Neuve, Belgium were supplied. Two homopolymers PB 0300M, characterized by melt flow index of 4 g/10 min (190 °C/2.16 kg) and density of 0.915 g.cm^{-3}, DP 0401 with melt flow index 15 g/10 min (190 °C/2.16 kg) and density of 0.915 g.cm^{-3} and one copolymer PB 8640M with melt flow index 1 g/10 min (190 °C/2.16 kg) and density 0.906 g.cm^{-3} were used. [5]

2.2 Sample preparation

Specimens designed for density measurement were prepared by compression molding from pellets of PB 0300M. Three plates (with dimensions of 12.5×12.5 mm) with various thickness 2, 1 and 0.5 mm were used. Plates were compression molded using hand-press at temperature of 170 °C for 5 minutes than cooled in hydraulic press at temperature of 60 °C for 10 minutes. Then, small specimens were cut out from the sheet and they were stored at given temperature.

Extruder Brabender Plasti-Corder PLE 651 was used for extrusion of tapes from all grades of PB-1. The processing conditions were following for all materials: compression ratio of the screw 1:4; screw speed 20 rpm; barrel temperatures 135, 140, 145, 150 °C, extrusion slit die with profile 2×20 mm with temperature 150 °C. Thus prepared tapes were cut out to specimens with dimensions (length×width×thickness) 160×20×2 mm for tensile testing. The same specimens with length of 50 mm were used for density measurement and WAXS.

The prepared specimens were immediately after processing annealed at various temperatures: -22, 5, 22, 40 and 60 °C at atmospheric pressure for various times. Two ovens (BinderBD23) with temperatures of 40 and 60 °C, refrigerator and freezer with common temperatures of and -22 °C were employed for annealing of specimens. Temperature of 22 °C was in the laboratory room.

2.3 Wide angle X-ray scattering

For scattering in the transmission mode, diffraction angle with interval $2\theta = 7–25°$, the measuring step of 0.05° and holding time of 5 s were used. A URD6 diffractometer CuKα radiation monochromatized with a Ni filter ($\lambda = 0.154$ nm) was employed for measuring of PB-1 extrudates in reflection mode. Whole extrudates of material PB 0300M with dimensions 2×20×50 mm were used as specimens for scattering.

The PeakFiT v4 was used for the evaluation of crystalline part in the samples. Furthermore, the content of the forms I and II during phase transformation was calculated by following the modified study of Marigo et al. [6]

2.4 Density measurement

Compression molded specimens were cut from sheets of different thicknesses (2, 1, 0.5 mm) to dimensions 35×20 mm. Each set of prepared specimens with three various thicknesses was annealed at given temperatures. Dimensions of extruded specimens for density testing were 35×20 mm with thickness 2 mm. Specimens from each of material were stored in the same conditions as compression molded samples. The material DP 0401M was annealed only at temperatures of 22 and 60 °C.

Density measurement correspond with the Standard ČSN 64 0111. The hydrostatic method was applied. The principle of immersion method is determination of density in small plastic specimens. For this method a digital scale, KERN 770 was used. As an immersion liquid, denatured ethanol was used. The density of the alcohol was measured by pycnometry.

2.5 Tensile testing

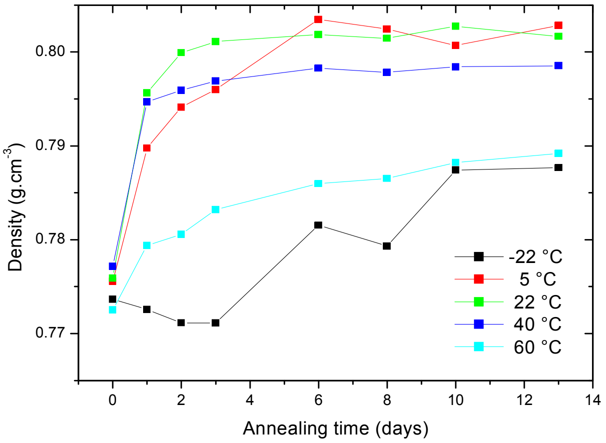
Mechanical properties, tensile properties of the specimens were measured by Zwick 145665 tensile tester. The tensile characteristics were evaluated by tester internal software TestXpert V7.11. Five specimens (average values are reported) from each material for each temperature were tested with constant speed 100 mm/min. Stress at break was derived from the stress–strain traces. Besides, the elastic modulus was evaluated using a Zwick external extensometer (gauge length of 20 mm) at a test speed of 1mm/min.

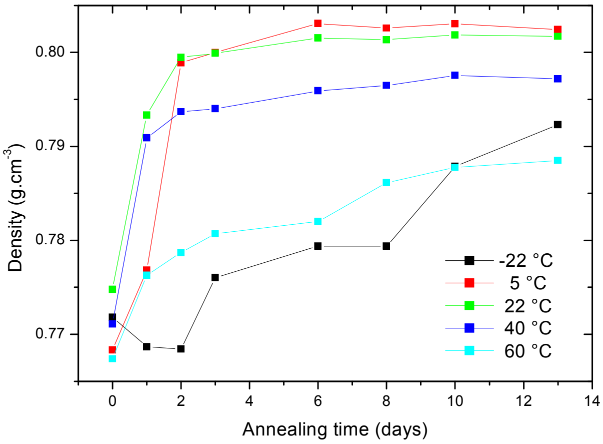
Specimens from each of material were measured during annealing time of 86 days. Five specimens of each material and all five temperatures were tested. Specimens were cut out the long tape after cooling. Dimensions of these specimens were length 160 mm, width 20 mm, and thickness 2 mm. Consequently, specimens from PB 0300M and PB 8640M were annealed to the five different temperature places -22, 5, 22, 40 and 60 °C. DP 0401 was exhibited to -22, 60 and 22 °C.

These extruded specimens were compared with studies of Beníček et al. (2008). Beníček et al. (2008) studied the thermal-induced transformation of injection-molded PB-1. The same grades of PB-1 (PB 0300M, DP 0401M, and PB 8640M) were used. These specimens were also annealed at the same temperatures of -22, 5, 22, 40, and 60 °C for annealing time of 0–48 days. [7]

3 Results and discussion

In this study, the physical properties were measured via density changes of specimens. It was found that densities of extrudates increase with rising annealing time in all grades of PB-1 at all annealing temperatures except -22 and 60 °C in PB 8640M and the fastest evolution occurs at temperatures of 5 and 22 °C in all materials. In the density evolution of compression-molded specimens increasing trend in evolution was observed and it is virtually the same evolution as could be seen in the extrudates. Different values of density show specimens annealed at -22 °C for all three thicknesses of the compression-molded specimens in comparison with the extrudates. It can be seen (Fig. 1) that the different thicknesses of compression-molded specimens does not influence the evolution of the density in compression-molded specimens respectively the rate of the phase transformation.





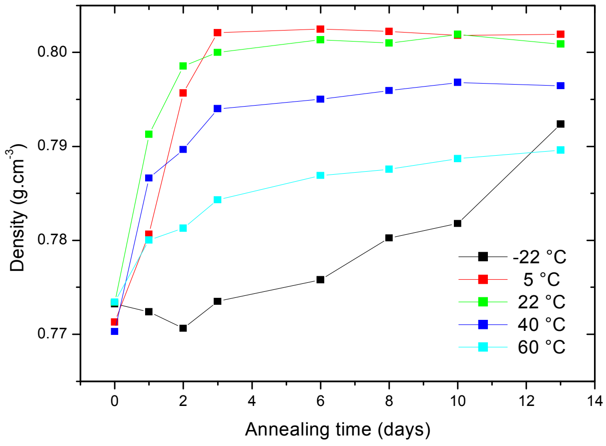


Fig. 1 Evolution of density in compression-molded specimens with thickness of 0.5 mm, 1 mm, 2 mm (down from top) of PB0300M

By WAXS it was investigated that the content of the form I increases with increasing annealing time (Fig. 2). During initial five days, the fastest increase of the form I was observed at temperatures of 5 and 22 °C. This observation follows those from density measurements. A specific behavior shows only specimen annealed at -22 °C with gradual increase of form I content du during initial fifteen days, followed by rapid increase to the values between annealing temperatures of 40 and 22 °C.

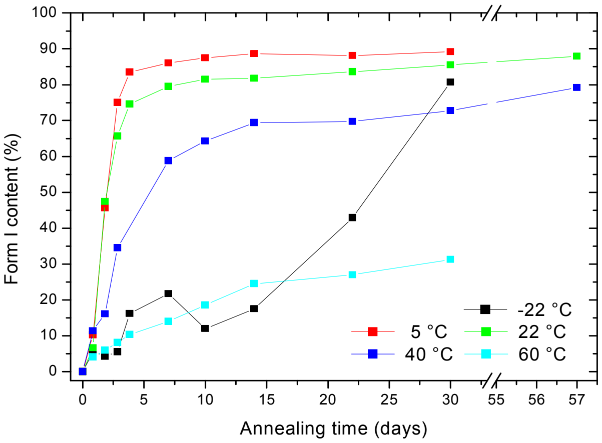


Fig. 2 Evolution of form I content in PB 0300M

When tensile modulus of material PB 0300M (Fig. 3) is compared to the form I content calculated from WAXS (Fig. 2) it can be seen that the trends are practically the same. Thus, the suggestion with a minimal critical amount of the form I it seems to be relevant. Also, the evolution of the phase transformation measured from the evolution of tensile modulus is a suitable method. The comparison with density measurements is limited, nevertheless the main trends are observed as well.

Tensile testing was performed in order to observe the evolution of tensile properties during the phase transformation in extrudates, which are commonly processed from PB-1. In extrudates it was observed in all materials that tensile moduli increase with increasing annealing time, see Figure 3. During initial seven days the increase of moduli is remarkable, especially at annealing temperatures of 5 and 22 °C. For these specimens plateau is achieved from the thirtieth day. Values of moduli in homopolymers are significantly higher than for ethylene copolymer (PB 8640M). Generally PB-1 possesses higher tensile modulus than polyethylene and as a result of copolymerization a lower modulus is expected.

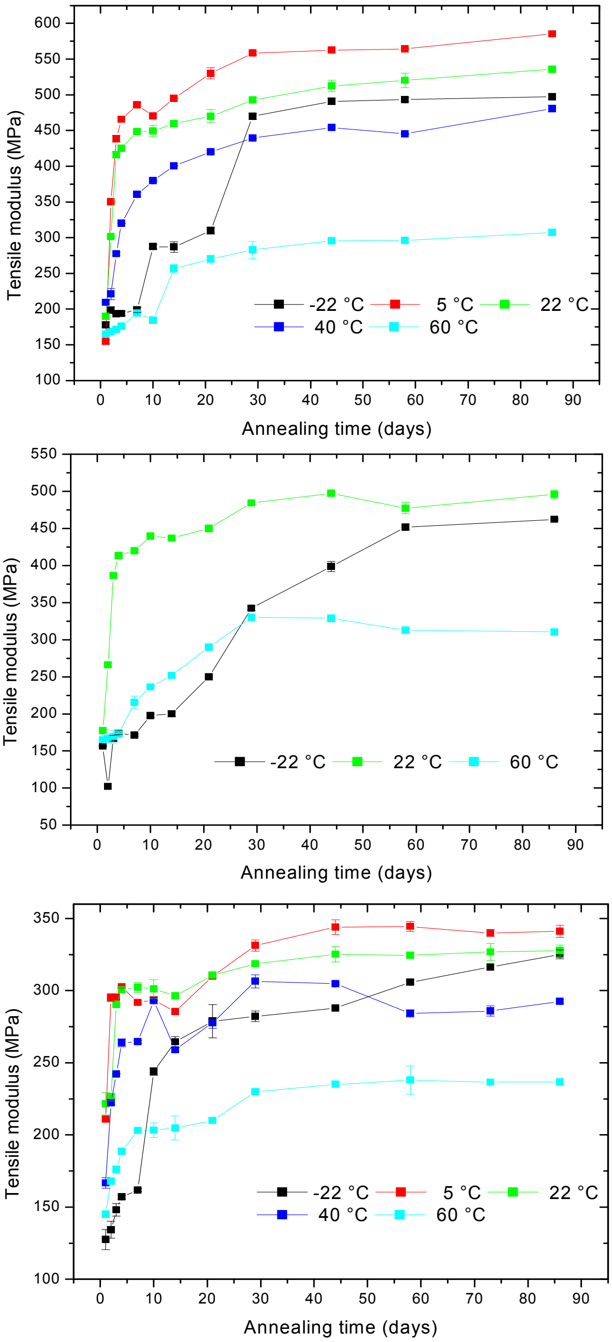


Fig. 3 Evolution of tensile modulus in extrudates of PB 0300M, DP 0401M and PB 8640M (down from top)

This material also transforms more readily than homopolymers as was observed in recent studies Beníček et al. (2008) and Beníček (2009). Beníček et al. (2008) found that the non-monotonic evolution of tensile modulus in dependence on annealing temperature is obvious. In all materials, the fastest evolution is evident at temperature of 6 and 22 °C, followed by a bit slower evolution at temperature of 40 °C. At annealing temperatures of -22 and 60 °C slow evolution was observed without rapid increase at -22 °C. As written above, copolymer PB 8640M possesses higher transformation rate and thus at annealing temperature -22 °C an increase of modulus is observed – remarkably later than in extrudates. Further important remark is that values of moduli in extrudates are remarkably higher than in injection-molded specimens (Fig. 3, 4). The morphology of extrudates possesses only spherulitic structure while in injection-molded specimens a typical skin-core morphological structure is achieved. These findings show a significant influence of processing on the rate of the phase transformation in PB-1. [7, 8]

When the evolution of tensile strength at break is discussed it is obvious that tensile strength at break decreases with increasing annealing time in all materials. Minimum values are observed after thirty days in case of both homopolymers (DP 0401M and PB 0300M). The evolution in copolymer PB 8640M is remarkably different where values vary. Again, the fastest evolution was observed at annealing temperature of 5 and 22 °C in all materials. When evolutions of extrudates and injection-molded specimens from PB 0300M are compared the opposite trend can be seen. Evolution of tensile strength at break in injection-molded specimens gradually rises with increasing annealing time [8], while evolution of tensile strength at break in extrudates decreases with increasing annealing time. It can be seen in case of PB 0300M that values from both sets of specimens converge to a plateau with the virtually same value. This is further evidence of influence of processing conditions on evolution of mechanical properties of PB-1.

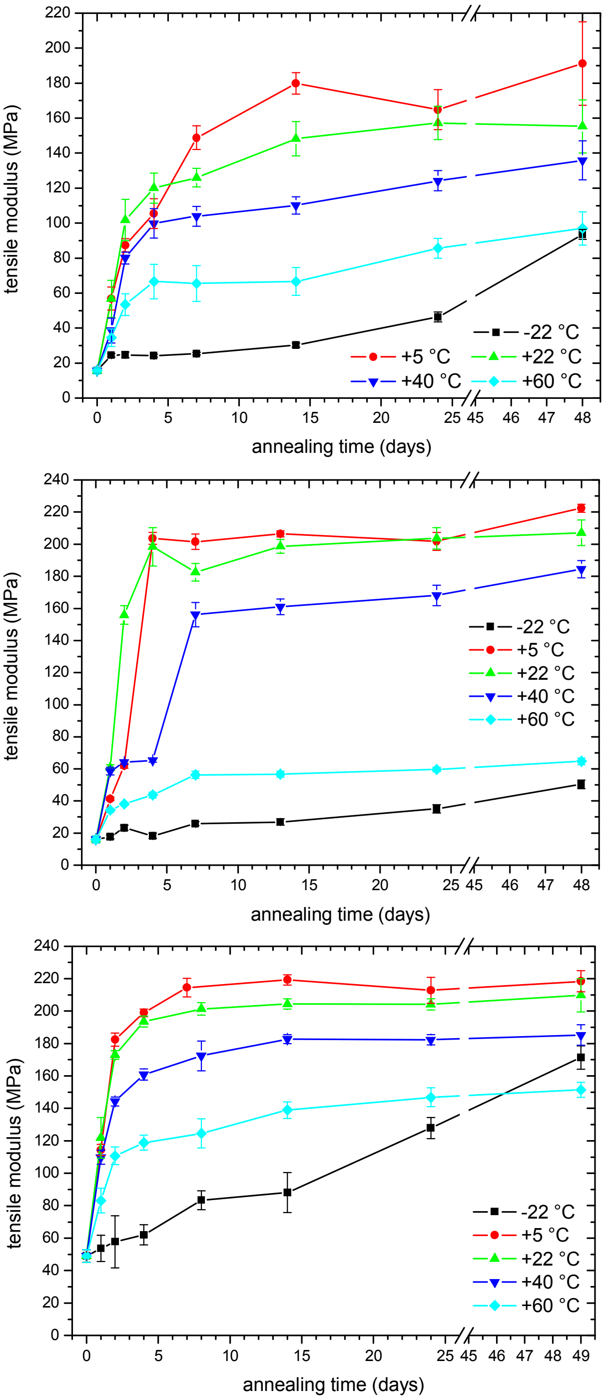


Fig. 4 Evolution of tensile modulus in injection-molded specimens of PB 0300M, DP 0401M and PB 8640M (down from top)

4 Conclusion

Form results of density measurements it is obvious that the different thicknesses of compression-molded specimens does not influence the evolution of rate of the phase transformation Densities of compression-molded and extrudates posses virtually the same values after the phase transformation. Probably, further measurement of density during the phase transformation would be desirable on specimens prepared under various crystallization conditions.

It was found that the content of the form I calculated from wide angle X-ray scattering increases with increasing annealing time and during initial five days fastest increase of form I was observed, nevertheless this observation was confirmed in testing of mechanical properties, this finding opens a question whether a critical minimum content of the form I accelerates the rate of the phase transformation at the lowest annealing temperature.

The study of evolution of mechanical properties was carried out on extrudates and consequently compared with injection-molded specimens. From observation it was apparent that values of moduli in extrudates were remarkably higher than in injection-molded specimens. Evolution of tensile strength at break in injection-molded specimens gradually has risen with increasing annealing time, while evolution of tensile strength at break in extrudates has decreased with increasing annealing time.

From observation of tensile characteristics it is evident that processing is a key parameter influencing mechanical properties and also the rate of the phase transformation.

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