THE EFFECT OF SOME PHYSICAL FACTORS ON THE PHASE STRUCTURE OF ISOTACTIC POLYBUTENE -1

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Abstract

Isotactic polybutene-1 (iPB-1) exhibits excellent physical, mechanical and chemical properties dependent on its most important polymorphic forms called form I, II and III. The most stable form I is generated via solid-state transformation of the tetragonal, kinetically favoured form II. The slow transformation rate of form II to I accompanied by sample shrink attains its maximum at 25 °C and takes 7 – 10 days which is a problem for iPB-1practical applications. Many attempts have been made to prepare the stable form I directly from the melt, or increase the II › I transformation rate but with a low success.

Introduction

Isotactic polybutene -1 is a polymer with good mechanical properties and excellent elastic recovery, resistant to many chemicals; physical, environmental stress cracking effects and high temperatures. These remarkable properties are affected by a relatively slow phase II › I transformation rate. The growth rate of iPB-1 crystalline phases was studied by Yamashita and Takahashi [9] who found that the growth rate of the phase I crystals is one hundredth that of phase II crystals around 75 °C.

The iPB-1 can exist in 3 main crystal modifications with a variety of helix conformations when subjected to different thermal and mechanical histories [1]. The kinetics of the II › I transformation occurs via nucleation at crystal form II sites and the transformation results in improving physical properties. The crystal fraction and crystal morphology does not change during the transition [2].

The two modifications (I and II) have different melting points and enthalpies [3]. The melting temperature shifts up about 10-15 °C. The X-ray diffraction spectra of three crystal forms of iPB-1 are shown in Figure 1. The form II › I transformation of iPB-1 is connected with densification and the crystal phase shrinking. The 11/3 helices of modification II are loosely packed, with a crystal density $\rho_{II} = 0.907$ g/cm^3 (T_{mII} = 128-131 °C) slightly higher density than that of the amorphous state, $\rho_a = 0.868$ g/cm^3 ($T_g = -54,2$ °C). The chain packing in the 3/1 helical modification of phase I corresponds to a crystal phase with a much higher density, $\rho_I = 0.95$ g/cm^3 ($T_{mI} = 141$ °C) and iPB-1 crystals reduce their volume by ~ 4%. The volume reduction of the crystal phase increases the strain to the attached amorphous chain portions at the crystal-amorphous interface.

Kopp et al. [6] crystallized the phase I in the melt via epitaxy on aromatic acids or salts crystals, and demonstrated that the phase I can grow in the thin melt even under atmospheric pressure. Powers *et al.* [7] used phase I, ob-
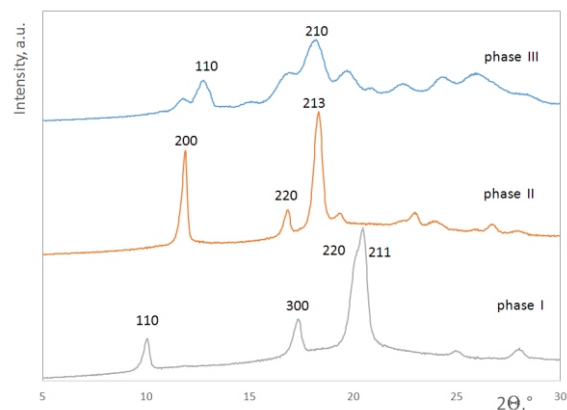
Figure 1. X-ray diffraction spectra of the 3 crystal forms of isotactic polybutene -1.

tained by solid-state transformation from phase II, as nuclei for phase I and expected to observe the growth of phase I crystals directly in the melt. This was not successful and Powers et al. [7] supposed that the growth rate of phase I crystals is exceedingly slower than that of phase II. Zhang *et al.* [8] found that at an elevated temperature of 110 °C the phase I crystals can be obtained from iPB-1 molten ultrathin films at atmospheric pressure. Yamashita and Takahashi [9] demonstrated that phase I can grow in the thin film melt via self-seeding at atmospheric pressure using solution-grown phase I crystals as nuclei. Some solid nucleating agents were partially successful mainly in drops or thin films. Lu and Yang refer [5] even on stabilization of phase II of iPB-1 by evaporated carbon.

Phase III has mainly a theoretical importance because it can be prepared only from iPB-1 solutions [17].

Experimental

Samples. Isotactic poly(butene)-1 (iPB-1) samples, solution polymerized using Ziegler-Natta heterogeneous catalysts, were the commercial products of LyondellBasell (Netherlands) including the homopolymers 110, 300 and 400. The samples 110 and 300 have a higher molecular weight than the 400 (according to the melting flow index measurements, see Table I.). Three kinds of copolymers with ethylene were also studied (samples 8640, 8510 and 8340). All substances were in p.a. quality.

X-ray diffraction. Wide angle X-ray diffraction patterns were measured using a PANalytical X-pert Prof X-ray diffraction system (Netherlands). The CuKα radiation was Ni-filtered. The scans (4.5° 2θ/min) in the reflexion mode were taken in the range 5-30° 2θ. The total sample crystallinity X was calculated from the intensity ratio of the crystal diffraction peaks and the amorphous background areas. The fraction of phase I in the X value was deter-
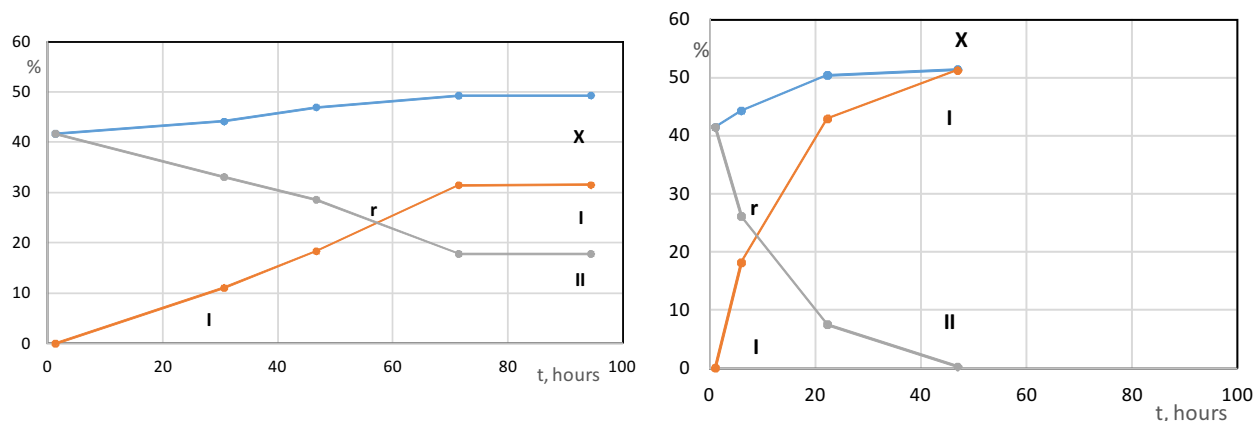
Figure 2. Phase transformation of the phase II to I – sample 110 in H$_2$O vapors (left), phase transformation of the phase II to I – sample 110 in xylene vapors (right).

mined comparing the crystal peak intensities of each form I and II. The *r* value (transformation half-time) represents the time when the % I during transformation equals the % of the untransformed phase II (Fig. 2a,b).

The effects influencing the II › I phase transformation of iPB-1

The phase transformation rate can be affected by several major factors, which can be divided into following categories:

A. The polymer structure

1. The molecular weight (based on melt flow index measurements) has a low effect on the transformation rate. The transformation rate of sample 110 with the higher molecular weight have the *r* value only 10% lower than samples 300 and 400 measured in H$_2$O vapous environment. It can be expected that a larger molecular chain could contain a larger number of chain defects representing the phase transformation nuclei.

2. The increased transformation rate was found in some iPB-1 copolymers, mainly with ethylene [12]. The higher transformation rate was found in samples with a higher ethylene content (e.g. 8510, *r* = 0,03 h). In case of a low ethylene content copolymers the rate changed to *r* = 10 h (in 8640) or 20 h (in 8340) in comparison with *r* = 39 h for homopolymer samples 110 and 300 with a higher molecular weight.

3. The effect of some melt prepared blends of iPB-1 was also studied and it was confirmed, that the addition of 5 % paraffin to the sample 300 did not influenced the transformation rate, but the same amount of linear polyethylene (LPE) increased the transformation rate twice (to 24 h). The blend preparation from solutions is complicated by the fact, that the solvent itself influences the transformation rate also. [4].

B. The effect of the melting conditions before crystallization

The melting conditions of the phase II crystallization inherently influence not only the phase II melt crystallization but also the following formation of the phase transformation nuclei.

1. A higher melting temperature led to a lower sample total crystallinity after the phase II – I transformation. The crystallinity decreased from 64 % (for melting at 125 °C) to 55 % (melting at 220 °C) in case of the sample 110; and from 68 % (melted at 130 °C) to 57 % (melted at 220 °C) for sample 400) and lead to a slower transformation rate *r* (in the sample 110 *r* increased from 16 h (at 120 °C) to *r* = 78 h (at 220 °C), respectively in sample 400 *r* = 46h (at 130 °C) and 70 h (at 220 °C).

2. Increasing the melting time at 160 °C to 8,5 hours resulted in decreasing the crystallinity X values from original 62 % to 58 % and increasing the transformation half-time *r* from 48 to 60 hours in case of sample 110. Similar results were found in case of sample 110 101 times successively repeatedly melted 5 min at 160 °C. Such behaviour is expected due to the effect of the decreased growth and secondary nucleation rate.

C. The effect of some physical factors on the phase II − I transformation

1. The study of the effect of the ambient temperature on the phase transformation rate proved that the optimum is around 25 °C. The higher or lower temperatures decreased the transformation rate [10].

2. Increasing pressure or sample deformation (e.g. by tension or twist) at the room temperature has a positive effect on the transformation rate [11].

The long-time elongation (during the whole transformation period) or a short time elongation (10 min) increase the transformation rate. In the sample 110, elongated short time at room temperature, the transition half-time decreased from 48 h to 2 h (for 10 % elongation) and to *r* = 0,5 h (for 20 and 30% elongations). The long term elongation in this sample results in *r* = 4 h (at 10% elongation) or *r* = 2 h (at 30% elongation). At a higher elongation temperature (80 °C) it was affirmed a permanent deformation without an increased molecular chain orientation in the elongation direction and so the transformation rate did not increase in such an extent as in the case of lower elongation temperatures. An example represents the sample BP 110 where at 80 °C and 10% elongation the half-time *r* = 6 h, at 20%

elongation r = 12,5 h and at 30% r = 11,5 h. Of course with increasing elongation the sample crystallinity decreased (e.g. at sample 110 and 10% elongation – the crystallinity was 59%) with the exception of long term deformation cases where, due to secondary crystallization the reversed growth of crystalline phase took place (e.g. 110 10% elongation – 62% of the crystalline phase) [18].

3. Application of nucleation agents or solid crystal additives used for primary crystallization was an obvious choice, because any recrystallization may involve heterogeneous nucleation. The attempts were only partially successful [4]. E.g. sodium salicylate increased the transformation rate maximally 2x [4]. On the other hand several anti-nucleation agents for the II › I transformation were found e.g. talc or Na_2CO_3, which decreased the transformation rate 2 or 3 times [4]. The effect of decreasing the phase transformation rate was noticed also in some environmental effects.

4. The electron and gamma irradiation of iPB-1 results mainly in chain scission [13-14], the effect on II › I transition is not reported uniformly [15]. Gamma irradiation resulted in both scission and cross linking but in a lesser extent than with polypropylene [16]. The beta irradiation of iPB-1 increases the transformation rate as can be seen on the sample 110 (in case of 0 kGy the r equals to 39h; in case of 198kGy irradiation dose the r is equal to 24 h).

5. Also the effect of direct electric current fields was studied and the preliminary results show that the increase of the electric field intensity lead to a higher transformation rate and to a slight increase of sample crystallinity. For the sample 110 the transformation rate increased up to r = 28,1 h (at 500V) and to r = 22,1 (at 1000V) [19]. The exact explanation and the effect of other fields is studied in the present time.

6. The transformation rate II – I is inevitably influenced by the environment, the r values varied in the range between 3 – 92 h according to the environment type. The most significant environmental effect on the transformation rate was observed in case of solvents. The vapours of good solvents increase the iPB -1 II – I transition rate significantly (r = 9-10 h) and also the phase transformation is complete as there are no remnant of the phase II.

In chemically neutral (air, acetone, ethanol) environments the transformation rate was in the range of r = 29 – 59 h, similar as in alcalic or acid vapours environment. The explanation of this effect is complicated by the fact, that in the term environment several factors may take place.

The most notable finding is that the important role in the phase transformation process plays the interaction of the solvent vapour with the sample amorphous phase. The solvent vapours dissolve in the sample amorphous phase, increase its segmental mobility and so support the phase transformation process. This effect of segmental mobility on the transformation rate was confirmed also in iPB -1 copolymers with ethylene or iPB-1 blends with linear polyethylene. It is evident that the most important role

Table I. Sample material characteristics of PB-1

Sample, Labeling	Density, g/cm³	Tm of phase I, °C	MFI, g/10min, 190°C/ 2.16 kg	Composition
110	0.914	128	0.4	PB-1 homopolymer
110 III		81. 94	0.4	PB-1 homopolymer
300	0.915	127	4	PB-1 homopolymer
400	0.915	126	15	PB-1 homopolymer
8640	0.906	113	1	random low P(B - 1/E) copolymer
8340	0.911	113	4	random low P(B - 1/E) copolymer
8510	0.897	94	40	random high P(B - 1/E) copolymer

represents the level of intermolecular forces between the environment elements and polymer.

7. The sample age as such significantly decreases the phase transition rate and the total crystallinity by intermolecular forces. The explanation could be in a time decreased segmental mobility. The lower crystallinity values are connected with a slow growth of amorphous phase at the expense of partially crystalline regions. All this resulted in a decreased phase transformation rate. The segmental order could be further influenced by another repeated melting. Here, the crystallinity did not change, but the transformation rate increased substantially compared to the situating after second melting. The transformation rate (r = 105 h) increased to r = 78 h for sample 110; or from r = 66 h to 40h for the 400 samples aged 11 years.

It is possible to notice that the structural changes characterizing the ageing process of iPB-1 are connected mainly with conformational changes in the amorphous phase. Taking into the account the relative large temperature distance from the polymer crystal melting temperature, the segmental mobility is limited to shorter chain segments which favours rather the conformation changes in the amorphous phase than the improvement of the crystalline phase order.

Conclusion

The phase transition of iPB-1 is influenced by several factors, which include mainly the process of nucleation and phase I growth. Except of the basic physical effects, which mainly speed up the phase transformation rate the effects of the environment either do not influence or significantly fasten or in few cases slow down the transformation rate. The practical importance has the effect of good solvent vapours which are able to shorten the II – I phase transformation time from usual tens to mere 1 – 2 hours.

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