Investigation of mechanical and thermal properties of oriented polyamid copolymer

A. M. Ádámné, K. Belina, M. Pósa, B. Kecskés

Kecskemét College, Institute of Metal and Polymer Technology – Kecskemét, Izsáki u. 10., H-6000, Hungary
 URL: www.gamf.hu   e-mail: major.andrea@gamf.kefo.hu;   belina.karoly@gamf.kefo.hu; posa.mark@gmail.hu

ABSTRACT: One of the important processing technologies is the vacuum forming. Complex deformation occurs in this process, and it influences the structure of the material. It is especially important in the case of crystalline polymers as the crystallisation usually occurs in oriented samples. Our research was carried out on vacuum formed PEBAX materials. Mechanical and thermal properties were determined as function of the orientation of the samples. We determined the crystallisation kinetics of the material in isothermal and in non isothermal conditions. It was found that the change of the modulus and the yield stress with the orientation is more or less follows the Hennig-rule. Thermodynamic melting point was determined by Hoffman-Weeks method. It was found that the Avrami-equation can describe the isothermal crystallisation kinetics in very wide range.

Key words: Thermoplastic elastomer, Crystallisation kinetics, Mechanical properties

1 INTRODUCTION

Packaging industry needs different types of materials to fulfil the different requirements. These materials should be relatively cheap and easily processable. This is the reason that polyolefines are the most widely used material in the packaging industry. However they have some disadvantages. Deformability of these materials is limited hence thermoplastic elastomers (TPE) are also used.

TPE's are block copolymers consisting of soft and hard segments. The soft phase has its glass transition temperature (or melting point if it is crystalline) below the service temperature. On the other hand, the glass transition temperature or melting point of the hard phase is higher than the room temperature. The separation of the two, usually incompatible part of the macromolecule is prevented by primary chemical bonds. These materials behave as cross-linked one at room temperature, but they can flow at higher temperature.

PEBAX is a thermoplastic elastomer consisting of linear chains of polyamide-12 blocks (hard segment) covalently bonded to polyether (polytetramethylene oxid) blocks (soft segment) by ester groups [1].

There are several papers reviewing different properties of polyamide thermoplastic elastomers [2-4]. It was found that the properties of these materials strongly depend on the chemical structure of them. Structural analysis shows that the PEBAX samples have microphase separation. The crystalline phase consists of polyamide blocks, while in the amorphous phase consists of polyamide and polyethylene oxide blocks. The melting behaviour of the materials depends on the polyamide content [2].

There are a little information in the literature on the change of the mechanical and thermal properties of elongated samples. In this paper we show our results of the mechanical and thermal properties of elongated PEBAX samples. Isothermal and non isothermal crystallisation was carried out and preliminary result of the thermodynamic melting point determination is also shown.

2 EXPERIMENTAL

Sheets of PEBAX 7033 SA 01 (Arkema) material

were used in the experiments. Thickness of the sheet was 1 mm. The sheets were signed with 10 by 10 squares. After the vacuum forming process, the size of the deformed squares gives information on the degree of orientation. Temperature of the sheet in the vacuum forming process was 210 ºC. Figure 1 shows a typical test sheet after vacuum forming.
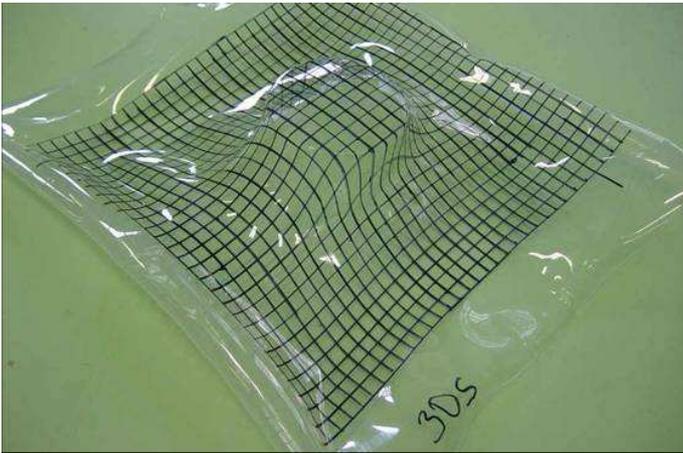

Fig. 1. Test sheet with signs after vacuum forming.

Thermal properties of the deformed samples were measured by TA Q200 DSC instrument in dynamic nitrogen atmosphere. The measured mass was around 1 mg. mass. The instrument was calibrated by Indium.

Tensile properties were measured by Instron 5566 tensile testing machine, 10 kN tension load cell. Test pieces correspond to ISO 527-2. The cross-head speed was 100 mm/min. Five parallels were measured, and the curves were averaged. The characteristic mechanical properties were determined from the average curve, according to Fig.2.
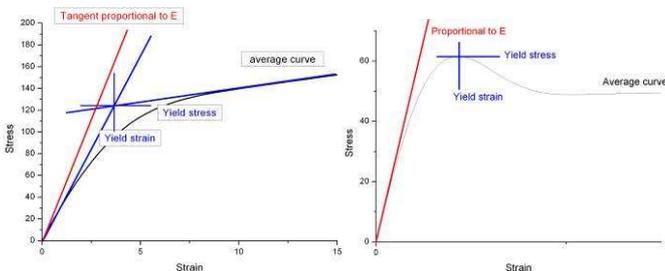

Fig. 2. Determination of the characteristic mechanical properties.

3 RESULTS AND DISCUSSION

3.1 Mechanical tests

The mechanical tests were carried out on the original and the deformed sheets. The measured tensile curves are different in the direction parallel to the production of the sheet and in the perpendicular direction (Fig. 3.).
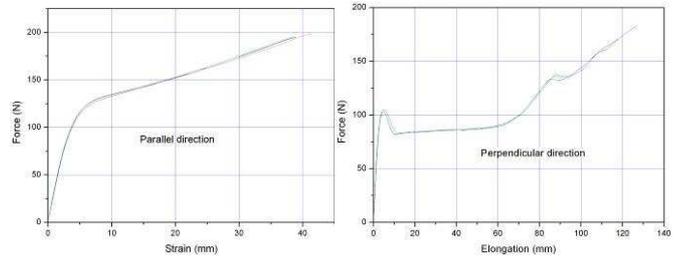

Fig. 3. Characteristic tensile curves in parallel and in perpendicular direction.

The measured yield stresses are shown in Figure 4. It is evident that increasing the orientation of the material, the yield stress increases in the direction of the orientation.
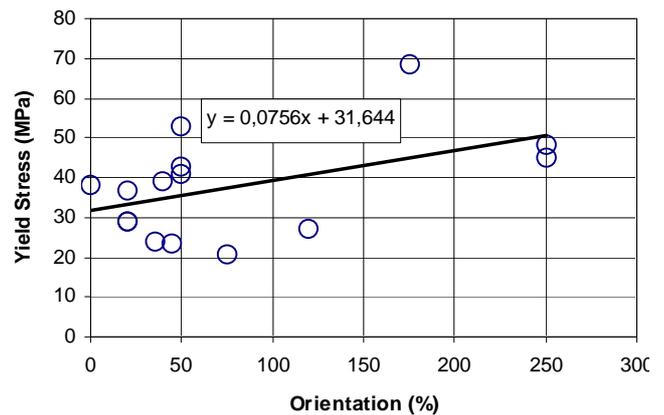

Fig. 4. Yield stress measured in the direction of the orientation.

On the other hand, the yield stress decreases in the direction perpendicular to the orientation (Fig. 5.).
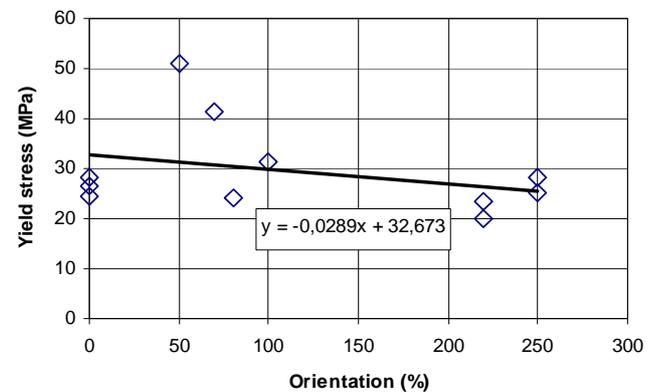

Fig. 5. Yield stress measured in the direction perpendicular to the orientation.

Similar change can be noticed in the initial slope of the tensile curves. These results are in relatively

good correlation with the Hennig rule stating that the increase of the mechanical strength is double than the decrease of it in parallel and perpendicular direction to the orientation, respectively.

3.2 Melting and crystallisation

Non isotherm crystallisation was carried out on the original material. The measured curves are shown in Fig. 6.
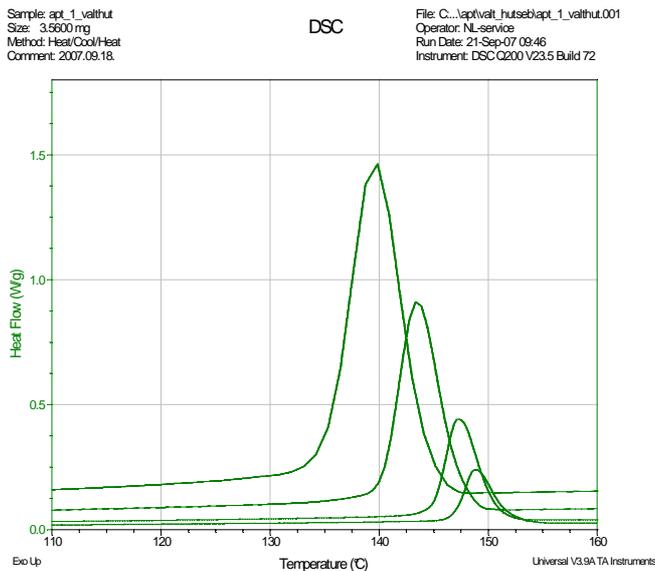

Fig. 6. Crystallisation curves of PEBAX 7033 SA 01 with different cooling rates (from left to right. V_c=10; 5; 2 and 1 K/min)

It can be seen that increasing the cooling rate, the crystallisation shifts towards the lower temperate range. The other important feature is that the crystallisation range is widening by the increasing cooling rate. At 1 K/min cooling rate the range is approximately 5 degrees, while at 40 K/min rate it is more than 10 degrees. Some instrumental factors could be involved in the widening of DSC peaks with increasing cooling rate.

The melting curves change with the cooling rate (Fig.7). Increasing the cooling rate, the melting curve shifts towards higher temperature region. It is well known that the crystal structure formed at high cooling rate thermodynamically less stable; the crystals are small and imperfect. On heating, these crystals can rearrange, forming a more stable form having higher melting point. In Fig. 7., it can be seen that the melting peak shifts from 170 ºC to 173 ºC as the cooling rate increases from 1 K/min to 10 K/min. Widening of the melting curve is also noticeable, supporting the structural change during the melting process.
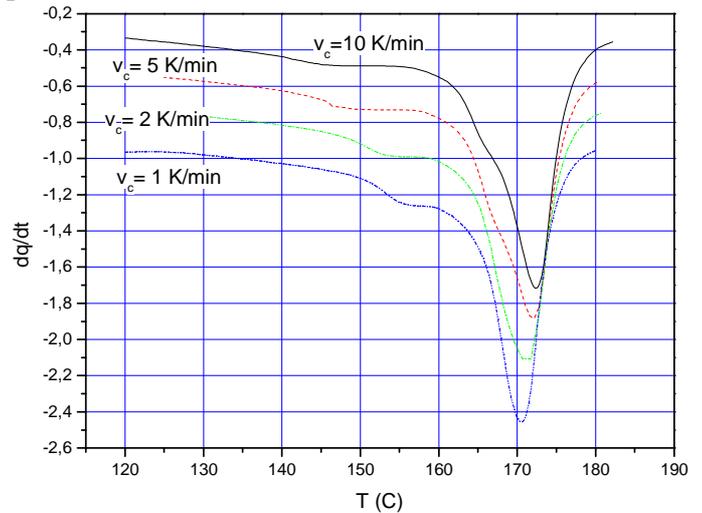

Fig. 7. Melting curves of PEBAX 7033 SA 01 material after different cooling rates. (The heating rate was 10 K/min.)

Isothermal crystallisation was carried out in a wide temperature range. The overall rate of crystallisation was determined by the Avrami equation:

$$x = 1 - \exp(Kt^n) \tag{1}$$

Where x stands for the relative crystallinity, K is the crystallisation rate constant, t is time and n is the Avrami's exponent. Fig. 8. shows the calculated curves.
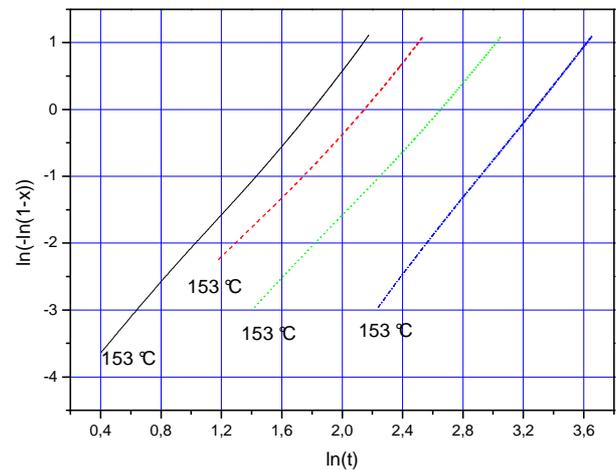

Fig. 8. Isothermal crystallisation curves of PEBA 7033 SA 01 material, using linear form of Eq. 1.

The calculated n and K values are summarised in Table 1.

Table1. Crystallisation rate constants and Avrami exponents at different temperatures

Crystallisation temperature (in °C)	n	ln(K))
153	2.64	-4,73
155	2.48	-5,28
157	2.47	-6,52
159	2.83	-9,25

The n value is between 2.5 and 3 showing athermal nucleation. As the crystallisation increases the rate constant decreases.

The melting curves of the isothermally crystallised samples are shown in Fig. 10.
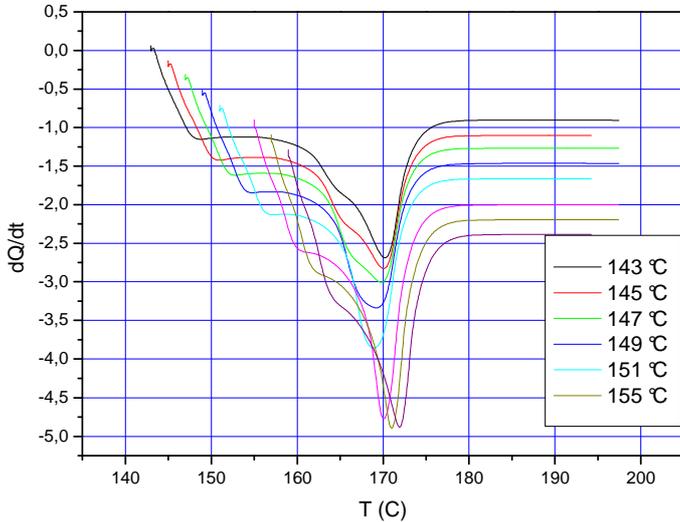

Fig.10. Melting curves of isothermally crystallised samples.

It can be seen that the melting curves shift to higher temperature as the crystallisation temperature increases. The higher melting point is due to the more perfect crystal structure formed at higher temperature. Using the Hoffman-Weeks equation (Eq.2), the thermodynamic melting point can be calculated:

$$T_m = T_m^0 \left(1 - \frac{1}{\gamma}\right) + \frac{T_c}{\gamma} \qquad (2)$$

Where T_m is the melting point, T_m^0 is the thermodynamic melting point, T_c is the crystallisation temperature, γ is the lamellar thickening quotient. We neglected the thickening of the lamella (linear approximation). The calculated thermodynamic melting point of the PEBAX 7033 SA 01 material is 189 °C.

4 CONCLUSIONS

PEBAX 7033 SA 01 material was characterised. Oriented samples were prepared by vacuum forming. Tensile measurements were carried out on the oriented samples. It was found that the tensile curves significantly different in the direction of orientation from the ones measured perpendicular to it. We found that the yield stress increases with the degree of orientation in the parallel direction, and decreases in the direction perpendicular to it. The change is more or less follows the Hennig rule. Non isotherm crystallisation measurements show that increasing the cooling rate the crystallisation range widens and shifts to lower temperatures. Overall crystallisation rate constants were determined from isothermal crystallisation by the Avrami equation. It was found that the nucleation of the process is athermal. Thermodynamic melting point was determined using the Hoffman-Weeks equation.

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