Research Article

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The crystallization and mechanical properties of poly(4-methyl-1-pentene) hard elastic film with different melt draw ratios

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Abstract: To study the effect of the melt-draw ratios (MDRs) on the structure and properties of the poly(4-methyl-1-pentene) (PMP) film, the crystal structure evolution and mechanical properties of the PMP film with an MDR of 40–160 were characterized using scanning electron microscopy, differential scanning calorimetry, wide-angle X-ray scattering, and mechanical test. The results show that with the increase of MDR, the spherulite to platelet transition occurs in the PMP. When the MDR exceeds 100, a parallel platelet structure appears. Due to the side chains, with the increase of MDR, the distribution density of tie chains in PMP decreases and the entanglement density of amorphous chains increases. This leads to a decrease in the yield strength and the strain hardening becomes noticeable. Although the crystalline network becomes loose due to the decrease in tie chain density, the elastic recovery (ER) value still increases with the increase of MDR. This result indicates that the entanglement density of the amorphous region greatly contributes to the ER.

Keywords: poly(4-methyl-1-pentene), hard elastic film, crystallization, uniaxial deformation, tie chain

1 Introduction

Usually, the polymer products are fabricated through a flow-induced crystallization (FIC) process, such as injection, extrusion, or melt extrusion casting (1). With the molecular chains extending, the crystalline velocity and nucleation density will improve. The crystalline structure transforms the spherulite to the lamellar structure (2). This transformation directly influences the mechanical properties of plastic products.

In the melt-extrusion casting process, the polymer melt is stretched between the extrusion die and chill roll and fast cooled by an air knife, and the melt strain rate is usually near 10 s^{-1} . The film usually forms a row-nucleated lamellar crystalline structure with some typical hard elastic properties, such as large modulus, high yield strength, and elastic recovery (ER) (3). Many semicrystalline polymers have been reported to fabricate such materials, such as polyethylene (PE), polypropylene (PP), polyvinylidene fluoride (PVDF), polyoxymethylene, and poly(4-methyl-1-pentene) (PMP) (4–8). In the past several years, as to the hard elastic material and its mechanical properties, compared with the linear structure polymers, less research has been done on polymers with branched chains. The effect of side chain groups on lamellar crystal formation and the corresponding mechanical properties in hard elastic system is still lacking attention.

In recent years, some studies of PMP hard elastic film have been reported (8–14). In the melt-extrusion cast process, the PMP crystalline lamellae would occur twisted to planar-like transformation with the *c*-axis orientation degree (f_c) increasing (13), but the lateral size of PMP lamellae is nearly of no change, which is different from PP or PE (8,15). However, even if PMP forms a highly oriented lamellar structure, its ER value is still very low (14). Apparently, the high-ordered arrangement of lamellar crystal is just a prerequisite for a hard elastic material, and it only provides a stable high strength skeleton. In fact, the ER behavior of hard elastic materials is determined by the

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cooperative motion of crystalline and amorphous regions (16,17). When the hard elastic material is uniaxial elastically deformed, the crystalline network is parallelly separated, and the amorphous molecular chain network will periodically change by extension and recovery. The arrangement of crystals and the entanglement of amorphous regions will affect the mechanical properties of hard elastic materials. Therefore, it is necessary to investigate the PMP crystalline morphology change in the FIC process and understand the effect of melt stretching on the entanglement network structure in the amorphous region, which will help us to understand the effect of melt draw ratios (MDRs, the ratio between the cast roll velocity and the extrusion velocity) on properties of PMP film.

2 Materials and methods

2.1 Materials

Extrusion grade PMP was supplied by Mitsui Petrochemical Ltd. (Japan) with a melt flow index of 9 g/10 min (260°C/5 kg). The melting point (T_m), obtained from differential scanning calorimetry (DSC, Mettler Toledo DSC3, Zurich) at a rate of 10°C·min⁻¹, is 234°C. The molecular weights are $M_n = 180,000$ g·mol⁻¹ and $M_w = 622,000$ g·mol⁻¹, measured by GPC (Viscotek model 350, Malvern Instruments Ltd, UK).

2.2 Preparation of PMP casting films

The cast films were prepared by extrusion casting through a T-slot die. During extrusion, the uniaxial (machine direction [MD]) stretching was applied to PMP melt, resulting in the oriented crystalline structures. The die and chill roll temperatures were set at 270°C and 100°C, respectively. The melt-draw ratios (MDRs) were set at 40, 80, 102, 139, and 164, respectively. The film thicknesses were 50, 40, 30, 18, and 15 µm, respectively.

2.3 Characterization

2.3.1 Scanning electron microscopy (SEM)

The surface morphology was characterized by SEM (S3400N, Hitachi, Japan). To observe the crystal structure clearly, the cast films were etched for 4 h at 80°C. A solution of 0.4 wt%

chromium trioxide in the blends of water and concentrated sulfuric acid was used as the etchant. The etched samples were then sputtered with a platinum ion beam for 300 s before test.

2.3.2 DSC

The thermal behavior was observed using a DSC (Mettler Toledo DSC3, Zurich). The temperature was raised from 60°C to 270°C at a rate of 10°C·min⁻¹ in N₂. The crystallinity was calculated based on the enthalpy change values obtained during the heating process, supposing a heat of fusion of 65.4 J·g⁻¹ for 100% crystallized PMP (8).

2.3.3 Wide-angle X-ray scattering (WAXS)

WAXS was carried out on the X-ray scattering station with Mar 345 image plate (3,070 × 3,070 pixels with a pixel size of 150 µm) as a detector and with a wavelength of 0.154 nm in National Synchrotron Radiation Laboratory in Hefei (China). The sample-to-detector distance was calibrated to be 355 mm, and the data-acquisition time for each frame was 300 s. The crystalline orientation was obtained by examining the azimuthal angle dependence of different reflections arising from standard flat-plate WAXS patterns.

The Herman's orientation factors of a , b , and c crystallographic axes of PMP crystal at different MDR values were calculated by the following equation (18,19):

$$f_j = \frac{3\langle \cos^2 \theta_j \rangle - 1}{2} \quad (1)$$

where j represents the a , b , and c crystallographic axes of the unit cell. The angle between the j crystallographic axis and the fiber axis is θ_j .

2.3.4 Test of tensile properties and ER

The stress-strain curves and ER were tested using an H&P Inspekt table blue machine equipped with a heating chamber at a deformation rate of 50 mm·min⁻¹. The stretching temperature was set at 60°C, 15°C higher than the glass transition temperature (T_g) of PMP (45°C).

The volume fraction of tie chain (β) was calculated according to the method proposed by Takayanagi (20):

$$\beta = \frac{(1 - X_c)E}{E_c - X_c E}, \quad (2)$$

where X_c is the crystallinity from the DSC test, E is the elastic modulus from the stress–strain curves, and E_c is the modulus of the crystalline part. Here, the modulus of tie chains was supposed to be approximate to that of the crystalline part, and 6.7 GPa was used (21). The elastic modulus of amorphous region E_a was neglected since the stretching temperature was higher than T_g .

The two times loading experiment was also tested to obtain the ER and the relaxation stress. The sample was first stretched to 50% at 50 mm·min^{−1} and kept taut for 40 s. Then, the sample was relieved and relaxed for 90 s. Finally, the sample was stretched for the second time. The stretching cycle was repeated. The percent elastic recovery was calculated by the following equation:

$$E_R = \frac{L - L'}{L - L_0} \times 100\%, \quad (3)$$

where L_0 is the initial length of the film before the extension, L is the length when strained to 50%, and L' is the length at the end of the extension.

3 Results and discussion

3.1 The effect of MDR on the crystallization of PMP hard elastic film

Figure 1 shows the surface morphology of etched PMP films prepared at different MDRs. The MD is given by the arrow. At MDRs less than 102, pronounced spherulite structure can be obtained. At an MDR of 102, a part of spherulites transforms to the lamellar structure. Furthermore, increase in the MDR value results only in the planar lamellar structure. This morphology transformation process is similar to that in PP and PVDF cast films (6,17), whereas it is not reported in Ma's work (9). At the same time, the lamellae turn shorter and sparse, which may be related to the fast crystal nucleation at the higher cooling rate and stretching velocity (21). The increase in nucleation density enhances the probability of crystal growth termination when neighboring lamellar crystals touch each other.

Figure 2 shows the DSC curves of PMP films prepared at different MDRs. The melting range is broadened at first and then turns narrow. This transformation zone is just corresponding to the spherulitic–lamellar crystal transformation region. The polydispersity of lamellar size induces the widening of the melting range. With the MDR increasing, the lamellar size turns homogenization, and this process narrows the melting range. All films show the melting point

Figure 1: SEM of etched PMP films prepared at different MDRs.

at around 232°C. The crystallinity increases from 59.5% at an MDR of 40 to 62% at an MDR of 164. The results show that improving MDR accelerates the crystalline velocity (22).

To furthermore describe the crystalline structure change, the PMP films are characterized by WAXS, as shown in

Figure 2: DSC curves of PMP casting film with MDR from 40 to 164.

Figure 3. Considering the crystalline orientation along the MD, the integrated curves along the meridional and equatorial direction are given, respectively, as shown in Figure A1 (in Appendix). The insert picture in Figure A1 means the integral area. Along the MD, typical diffraction peaks appear at 2θ value of 9.5° , 13.4° , 16.6° , 18.5° , and 21.5° , corresponding to (200), (220), (212), (312), and (322/203) crystalline planes (23), which are the typical diffraction peaks for crystalline phases form I (24,25). With the MDR increasing, the intensity of the amorphous region turns weak, which indicates that the melt-stretching force induces the improvement of amorphous chains arrangement. But, in the transverse direction (TD), the (200) peak gradually weakens and disappears with the increase of the MDRs. This process is related to the sharp increase of the crystal orientation. Combining the diffraction integral signals in the MD and TD directions, we believe that there is no crystal rotation during the melt-stretching process, and this result is consistent with the above SEM results.

The Herman's orientation factors for the a , b , and c crystallographic axes of each sample are calculated by Eq. 1. For crystalline form I of PMP crystal, the (200) crystallographic plane is used to obtain f_a . Again $f_a = f_b$ due to the tetragonal unit cell structure, and f_c can be calculated as follows:

$$f_a + f_b + f_c = 1 \quad (4)$$

We follow the Herman's orientation factors of a , b , and c crystallographic axes at different MDR values. It could be clearly observed that with the MDR increasing,

the diffraction pattern of (200) plane transforms from a ring to a typical arc shape, meaning that the orientation of (200) plane turns stronger. The azimuthal integration of (200) plane was analyzed using FIT-2D software (European Synchrotron Radiation Facility, UK) and plotted against the azimuthal angle from 0° to 180° (as shown in Figure A2). With the augmentation of the MDRs, we could see the intensity of diffraction peak of the (200) plane is increased, and the peak turns narrow, implying a higher orientation of the unit cell arrangement under high MDR.

The values of the orientation degree at various MDRs are calculated as shown in Figure 4. At a relatively low MDR, the orientation degree is very low; also many spherulite structures can be seen in Figure 1. With the MDR increasing, the orientation degree along MD shows an obvious increase from 0.61 to 0.79, which conforms to the crystalline morphology transformation. This result is similar to Choi and White reported in a PMP melt-spinning process (26,27).

3.2 The effect of MDR on the crystallization of PMP hard elastic film

The true strain–stress curves of PMP films at 60°C and the corresponding Haward–Thackray plots are shown in Figure 5. The model is shown as an inset in Figure 5b. The mechanical data are listed in Table 1, including the

Figure 3: WAXS-scattering patterns of PMP films prepared at different MDRs.

Figure 4: The Hermans' orientation degree of cast films prepared at different MDRs.

elastic modulus (E), network modulus (G), tie chain volume fraction (β), yield stress (σ_y), and ER (E_R). With the MDR increasing, the elongation at break turns small and the strain-hardening behavior enhances. It is interesting that the elastic modulus and yield stress are weakened with the MDR value increasing. This result is different from any earlier reported hard elastic materials (4–7). Compared with other materials, only PMP has a branch chain molecular structure. The existence of side chains may reduce the tie chain formation (28). During the cooling process, the molecular chains are fully extended in the melt-flow field. The side chains reduce the tie chain distribution, which makes the crystal network loose.

Table 1: The mechanical parameters of cast films prepared at different MDRs

MDR	40	80	102	139	164
E (MPa)	665	377	249	221	147
G (MPa)	2.1	3.4	4.4	4.7	—
β (vol%)	4.3	2.3	1.5	1.3	0.8
X_c (%)	59	59	60	61	62
σ_y (MPa)	15.8	14.5	9.9	8.5	7.2
ER (%)	27.8	37.5	41.6	43.5	44.8

Meanwhile, the crystalline structure transforms from spherulites to lamellar structure, making the lamellae crystal's shearing destroy weak during the extension process. The typical yield failure behavior which comes from the crystal deformation. From the WAXS data, we notice that the perfection of PMP crystal cell enhances with the increasing MDR. This indicates that the PMP crystals are difficult to destroy when the stretching temperature is higher than T_g .

The amorphous chain network modulus can be extracted using the Haward–Thakray model (29). This model can be described as a Hookean elastic spring in a series with an Eyring dashpot and a rubbery spring in parallel. All basic macroscopic structure evaluation during uniaxial stretching can be described by this simple model (30). The Hookean spring and dashpot correspond to the crystalline phase deformation and lamellae slipping in uniaxial stretching. The rubbery spring is related to the amorphous region deformation. Based on Haward–Thakray model, a plot of the true stress as a function of $\lambda^2 - 1/\lambda$ is given, and the amorphous region modulus can be calculated based on the slope of strain-hardening region. The amorphous region modulus enhances with

Figure 5: True stress–strain curves of PMP films with different MDRs at 60°C (a) and the corresponding Haward–Thackray plots (b). The model is shown as an inset in (b).

Figure 6: The relationship between yield stress and volume fraction of tie chains.

increasing MDR. This means that the chain entanglement density is enhanced with increasing MDR.

In addition, the relationship between the yield stress and volume fraction of a tie chain is given in Figure 6. With the MDR value increasing, the crystalline morphology transforms from the spherulite to the planar lamellar structure. The reduction of the tie chain volume fraction makes the connection between single lamellar crystal weak. The yield stress linearly reduces with the weakened crystal network. Apparently, the side chain inhibits the crystalline network formation. But, at very low MDR, the relationship between β and σ_y deviates from the linear relation. This is mostly because the spherulite

deformation is accompanied with the crystal slip and shearing destroy. In PP hard elastic film stretching process, we also found similar results (15).

The ER is an important parameter of hard elastic materials. With the increase of the MDRs, the ER value of PMP film gradually increases and the maximum value reaches 44.8%. Compared to other common hard elastic materials, this value is still very low. In general, we attribute the ER of hard elastic materials to elastic energy of the crystalline network connected by tie chains (15,31,32). From the above results, the weakened crystalline network would result in lower ER. But in Table 1, the ER increases with MDRs. The increase of the entanglement density of the amorphous region caused by the melt stretching also increases the ER. The contribution of the elastic deformation of the amorphous network to the ER of hard elastic materials cannot be neglected.

In the twice loading experiment, when the film is stretched and kept at 50%, there is an apparent stress drop, which is related to the molecule chain relaxation in the amorphous region (33). The relationship between stress drop in twice cyclic process versus MDR and amorphous modulus is given in Figure 7. It is shown that the stress drop in twice cyclic tensile processes is nearly no change, and the stress drop is linearly reduced with the amorphous network modulus turning small. In the strain-hardening region, the amorphous chain network acts as the main force unit. The relaxation process is mainly the adjustment of the molecular chain conformation and local relaxation in the amorphous region. The contribution of the crystalline region is almost negligible for the relaxation process.

Figure 7: The stress relaxation during two-cycle stretching of films prepared at different MDRs.

4 Conclusion

In this article, PMP hard elastic films are prepared by the melt-stretching method, and their crystallization and mechanical properties are studied. The results show that with the increase of the MDRs, PMP has undergone a transition from spherulite to a parallel-arranged lamellar structure. As the crystallization speed increases, the lateral size of the crystals decreases significantly. PMP only forms I form crystals during the melt-stretching process, and the orientation of the *c*-axis does not change significantly when the MDR reaches 100. At this time, the PMP film mainly exists in a parallel-arranged lamellar structure.

Due to the presence of side chains in the PMP molecular chain, the distribution density of the tie chain decreases with the increase of the MDRs, which makes

the yield strength and elastic modulus of the hard elastic film significantly lower. However, the entanglement density of the amorphous region has increased significantly, which makes the tensile hardening of the PMP hard elastic film obvious and also increases the ER. This result shows that for hard elastic materials, the crystalline network has a significant impact on the yield region, and the ER process does not merely rely on elastic energy from the elastic deformation of the crystalline network. The contribution of the network of amorphous regions to the hard ER is also important.

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Appendix

Figure A1: The integral curves of WAXS patterns along meridional (a) and equatorial (b) direction of PMP cast films prepared at different MDRs; the insert picture means the integral area.

Figure A2: The intensity of the (200) plane at different MDRs.