



# The study of room-temperature stretching of annealed polypropylene cast film with row-nucleated crystalline structure



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## ABSTRACT

The room-temperature stretching process of polypropylene annealed film with row-nucleated crystalline structure was studied by in-situ small-angle X-ray scattering (SAXS) setup and off-line wide-angle X-ray scattering (WAXS), temperature-modulated differential scanning calorimetry (TMDSC) and stress–strain curves testing. The formation process of initial connecting bridges and pores was clarified. For the annealed film, except for the initial lamellae structure, the recrystallized part formed by the melting and crystallization of imperfect crystals during annealing, tie chains connecting the lamellae structure among the amorphous region, secondary crystals from the crystallization of tie chains during annealing and daughter crystals from the special cross-hatched crystalline structure of PP coexist. It was found that 10% stretching lead to the pronounced increase of long period and the appearance of a few initial connecting bridges. The stretching of daughter crystal and recrystallized part contributed to the formation of initial bridges. At stretching ratio of 30%, uniform distributed connecting bridges were observed and the stretched film showed maximum structure periodicity. At this stretching ratio, except for the stretching of daughter crystal, the stretching of tie chains and secondary crystals within the amorphous region lead to the formation of more connecting bridges. At higher stretching ratios into the strain-hardening region and beyond the second yield point, except for the stretching of the above mentioned crystalline and amorphous structure, the stretching of mother lamellae occurred and lamellae deformation was inevitable, resulting in lower structure periodicity. During room-temperature stretching, the pores were formed progressively and the stretching ratio of 30%, situated at the transition point from plastic plateau to strain-hardening region in the stress–strain curves, was appropriate for the initiation of pores.

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## 1. Introduction

Based on melt-stretching mechanism [1], polypropylene (PP) microporous membrane has been successfully fabricated and used as a separator in the field of Lithium ion battery. The fabrication process mainly covers three stages [2,3]: (1) production of the precursor film with prerequisite row-nucleated lamellar crystalline structure, (2) annealing to thicken the lamellae and improve lamellae orientation and uniformity, (3) stretching of the film at room temperature for pores creation and then at high temperature

to enlarge the pores. After these, the heat-setting is carried out to improve the dimensional stability of stretched microporous membrane. There have been detailed works about the influence of the physical properties of raw materials, applied cast processing conditions and annealing technology on the crystalline properties and stretched pore structures [4–13]. However, as to the pore initiation process during room-temperature stretching, few works have been carried out to clarify how the initial pores are formed.

In the works by Carreau group in the field of PP microporous membrane, the room-temperature stretching ratio was set at 35–40% [7–11], based on the direct comparison of structure and properties of stretched microporous membrane. In our previous work [14–16], to follow the changes induced by room-temperature stretching, the room-temperature stretched films were heat-set at 145 °C for 10 min to decrease their shrinkage. This is since the

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annealed films show higher elastic recovery and the stretched film by only room-temperature stretching will recover to its unstretched state after the stretching stress is relieved. Compared with that of precursor film, the pronounced changes after annealing were the appearance of plastic plateau region in the stress–strain curve and an endotherm plateau in the differential scanning calorimetry (DSC) curve, which were related to the occurrence of secondary crystallization behavior from tie chains during annealing. It was found that when the room-temperature stretching ratio was set around the transition point from the plastic plateau region to strain-hardening region in the stress–strain curve of annealed film, the endotherm plateau in the DSC curve and the plastic plateau in the stress–strain curve disappeared, and the corresponding microstructure showed initial pores among the separated lamellae. Then it was proposed that the secondary crystals formed during annealing were transformed to the initial pores during the stretching process. Sadeghi et al. [8] summarized that the following phenomena took place simultaneously during room temperature stretching: void formation as a result of short tie chain scission, crystal block slipping and their reorienting along the stretching direction, stretching of longer tie chains as shorter tie chains were broken apart and crystallization of highly stretched long tie chains. Here, the pore initialization was attributed to the stretching and scission of short tie chains. Matsui et al. [17] used time-resolved simultaneous wide- and small-angle X-ray scattering measurements to follow the cold stretching process. The result showed that the voids appeared after the amorphous region were stretched, at the same time, the lamellae crystals were deformed by bending. Lin et al. [18] believed that the orientation degree of lamellae crystals and thickness of amorphous region in the precursor film were the main reasons affecting pores formation.

Generally, annealing is carried out at temperature around 145 °C. At this high temperature, some imperfect lamellae existing in the precursor film can be melted and recrystallized to more perfect crystals. At the same time, the tie chains among the amorphous region will crystallize through secondary crystallization. It is believed that the former behavior stabilizes the initial lamellar structure. In addition, for PP, the mother-daughter crystal phenomenon (i.e. cross-hatched crystal structure) naturally occurs. For this unique mother-daughter crystal structure, the daughter lamellae grow epitaxially on the (010) plane of mother lamellae at approximately 80° [19]. This special mother-daughter assembly actually enriches the basic deformation mechanism [20,21]. Nozue et al. [22] pointed out that during the deformation process of spherulite, the amorphous chains were elongated at first and then disordering of parent lamella crystals along a-axis and rotation of daughter lamellae were followed by fragmentation along perpendicular direction, whereas along the parallel direction, at the initial stage disordering of crystals occurred along a-axis, subsequently rotation of parent lamellae were followed by rotation of daughter lamellae. It is obvious that the existing daughter crystals significantly affect PP properties.

In the annealed film with row-nucleated crystalline structure, initial main lamellae, recrystallized region from imperfect lamellae, secondary crystallization from tie chains, daughter crystal and tie chains in the amorphous region coexist. This will complicate the stretching behavior of annealed film and the pore initiation process during room temperature stretching. In addition to the above mentioned relationship among secondary crystallization, short tie chains and the initialed pores, we want to know what will happen to the recrystallized region from imperfect lamellae and the daughter crystals during room temperature stretching. Is there any relationship among them and the pore initialization? This paper monitors the stretching process of annealed PP films with row-nucleated crystalline structure under room temperature. The

changes in crystalline structure and tie chains content were characterized. The pore formation process during room temperature stretching was discussed.

## 2. Experimental

### 2.1. Material

A homo-polypropylene resin with a melt flow rate value of 2.0 g/10 min (under ASTM D 1238 conditions of 230 °C and 2.16 kg) from Yangzi petrochemical company, China, was used. The melting peak point ( $T_m$ ) and crystallinity, obtained from differential scanning calorimetry (DSC; PerkinElmer DSC, Massachusetts, United States) at a rate of 10 °C/min, were 164.2 °C and 39.0%, respectively. The reported crystallinity results were obtained using a heat of fusion of 209 J/g for fully crystalline PP [7]. The weight-average molecular weight and polydispersity index, measured using a GPC (Viscotek model 350) at 140 °C and 1,2,4-trichlorobenzene (TCB) as a solvent, were about 754 kg/mol and 6.29, respectively. The xylene soluble content at room temperature was less than 4%.

### 2.2. Annealed and stretched film preparation

The precursor film was prepared by cast extrusion through a T-slot die followed by stretching and thermal-setting. During extrusion, the uniaxial (machine direction, MD) stretching was applied to PP melt, which resulted in the oriented crystalline structures. The die temperature was set at 210 °C and a draw ratio of 125 was applied. The draw ratio was determined by the take-up speed, since the extrude velocity at the exit of the die was constant. The films were produced at chill roll temperature of 80 °C. Then the prepared precursor film was annealed for 30 min at 145 °C in a hot oven to obtain the annealed film. The thickness of annealed film is 25 μm.

To follow the microstructure change during room-temperature stretching, the annealed film was also stretched using an Instron 5500R machine equipped with a heating chamber to different ratios at 50 μm s<sup>-1</sup> and then the stretched structure was kept by heat-setting the films at 145 °C for 10 min to avoid the shrinkage of the film. Fig. 1 shows the stress–strain curve of annealed film during room temperature stretching. The stretching ratios were set at 10%, 20%, 30%, 50% and 110%, respectively. The former two ratios were within the plastic plateau region. 30% stretching ratio was around the transition point from plastic plateau region to strain-hardening region. 50% was within the strain-hardening region, whereas 110% was beyond the second yielding point. The thickness of film

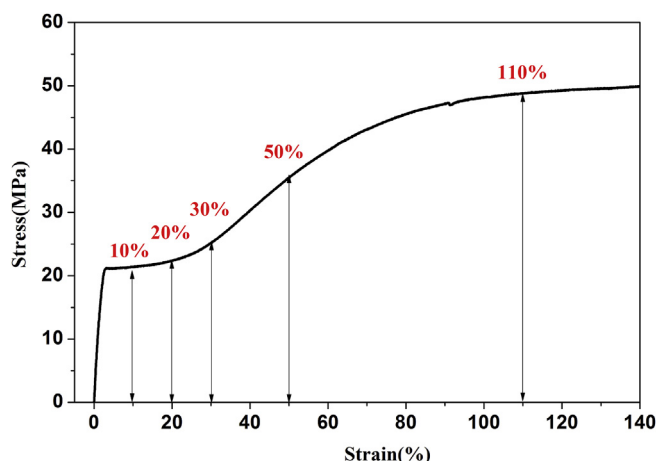


Fig. 1. The stress–strain curve of annealed film during room-temperature stretching.

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