

Morphology of fibers formed via thermally induced phase separation of polypropylene and liquid paraffin blend in stress-field

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Summary

Phase diagram obtained from small angle light scattering (SALS) and differential scanning calorimetry (DSC) of polypropylene/liquid paraffin blend system indicates that the melts undergo solid-liquid phase separation upon cooling and liquid paraffin is expelled out of crystalline region of polypropylene. Fibers spun under high take-up draw ratio are found to be hard-elastic. Long periods in the meridional direction are observed on the curves of small angle X-ray scattering (SAXS), and the yield point of fibers decreases with the increase in liquid paraffin content, which indicates such fibers have row-nucleated lamellar structure perpendicular to the fiber direction. The feasibility of preparing microporous membranes by stretching such fibers is investigated.

Introduction

The thermally induced phase separation (TIPS) process has been utilized for making microporous materials, such as membranes and foams, from semicrystalline polymers [1-4]. Depending on the polymer-diluent interactions, there are three different phase separation mechanisms in the TIPS process: solid-liquid TIPS (that is, the polymer crystallizes from the melt-blend), liquid-solid TIPS (crystallization of the diluent from the melt-blend, followed by the crystallization of the polymer), and liquid-liquid TIPS (that is, the formation of a polymer-rich liquid matrix and a dispersed polymer-lean liquid, with subsequent solidification of the polymer). In solid-liquid TIPS, crystallization of the polymer is spherulitic and the morphology is determined by crystal nucleation and growth [9]. Spherulites start by growing from a nucleus into lamella, the lamella then spawn into sheaf-like structures called axialites [5-7] which then develop into spherulites. The space between crystalline domains become the pores upon the extraction of the diluent. Polypropylene is one of the most popular TIPS membrane materials because of its many advantages over other polymers [8], and TIPS of polypropylene with various diluents have been investigated: liquid paraffin [9], dotriacontane [10], cyclohexanol [11], hexamethylbenzene [12], etc.

It is well known that semicrystalline polymers melted spun in a stress field under high take-up ratio have a row nucleated structure of stacked lamellae normal to the fiber direction, *and upon annealing polymers with good elasticity can be obtained.*

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Such polymers are named as springy, or 'hard-elastic' polymers [13-15]. *Typically, annealing temperature range is 12~140 °C for obtaining hard elastic materials*[16]. The mechanism of the formation of such structure has been investigated by J.E.Spruiell et.al.[13,14]. By extension of hard-elastic polymers microporous membranes were obtained [17,18].

Up to now, however, there has been no report of the morphology of the thermally induced phase separation of polymer-diluent system in a stress field. In this work morphology of polypropylene/liquid paraffin blend crystallized in the stress field was studied. Elastic fiber was obtained from the blend melt spun with high take-up draw ratio. The feasibility of membrane preparation from such fibers was proposed.

Experimental

Materials

Isotactic PP with melt index 3g/10min, $M_w=4.46 \times 10^5$, $M_w/M_n=4.03$, was purchased from Shanghai Petroleum Chemical Co. Liquid paraffin was chemical pure reagent with boiling range 280~300 °C and used without further purification.

Blending and spinning

Blends of isotactic *polypropylene* and liquid paraffin were prepared in a Brabender mixer at 200 °C for 5 min, with rotor speed of 20 rpm. Fibers for studying crystalline structures were spun under different take-up draw ratio in a capillary rheometer at 200°C. The diameter of the capillary was 1.5mm, and fibers were cooled in static air bath of 25 °C and then annealed at 130 °C for 30 min. *Under this temperature fibers with good elasticity were obtained.* Hollow fibers were spun using a single-screw extruder (D:20mm, L/D:25) equipped with a gear pump at the spinneret temperature of 210°C. The outer diameter of the spinneret was 23 mm and the width of the circular gap was 2mm.

Phase Diagram Acquisition

Phase diagram was obtained by small angle light scattering (SALS) and differential scanning calorimetry (DSC) methods. In the SALS method, samples were placed in the hot stage of the scattering device at 200 °C for 6 minutes, then cooled to 100 °C at a cooling rate of 1 °C/min. The time when scattering began to appear was obtained by data processing software and converted to temperature. Whether such temperature was phase separation temperature or PP crystallization temperature was determined by microscope observation [21]. In DSC, the experimental condition was the same.

Charaterization of structure and properties

The stress-strain curves of fibers were obtained at 20°C with an Instron tensile tester modal 1121(strain rate:100% elongation/min). SAXS measurements were carried out at a Rigaku Dmax/rB X-ray diffraction device. The x-ray is Ni-filtered CuK_{α} from a fine-focus x-ray generator operated at 40KV x 100mA.

The fluxes of nitrogen gases through a hollow fiber module were measured by employing a soap bubble meter at a transmembrane pressure of 0.01MPa. The bubble point pressure was measured in an ethanol-water mixture (45vol% ethanol). Permeability coefficient was calculated according to reference 19. Porosity was estimated from the density of the hollow fibers.

Results and discussion

Phase diagram of PP/liquid paraffin system is given in Fig 1, which shows a typical solid-liquid phase separation diagram. At high temperatures polypropylene can be dissolved in liquid paraffin and form a homogeneous solution. When cooled to

certain temperature, crystallization of polypropylene begins which induces phase separation. Liquid paraffin is then expelled out of the crystalline region of polypropylene. In this phase diagram SALS and DSC results are consistent. *DSC is a thermometric method, however, thermal change is not intense during phase separation, therefore a temperature lag exists in this method. On the other hand, SALS method measures the change of light scattering during phase separation, which can be observed when the phase dimension is greater than the light wavelength. The size of detection of SALS is smaller. Therefore, a temperature difference between DSC and SALS experiments is observed.*

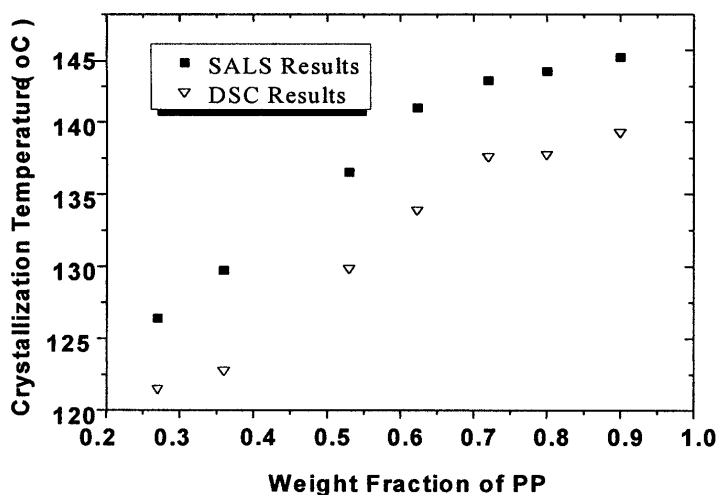


Fig.1 Phase diagram of PP/liquid paraffin system

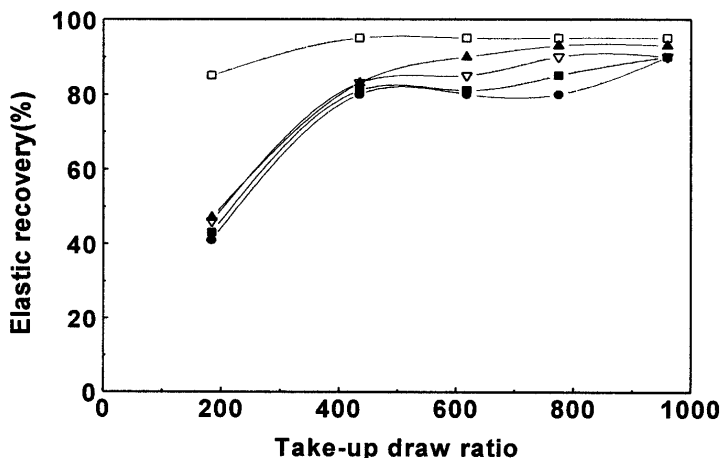


Fig.2 Relation between elastic recovery and take-up draw ratio with different liquid paraffin contents (paraffin content: (□):0% (▲):10%(▽):20% (■):30%(●):40%)

When virgin polypropylene is melted spun in a stress field, elastic polypropylene fibers with row-nucleated structure of stacked lamellae can be obtained, which is a characteristic of semi-crystalline polymers. Crystallinity of polypropylene decreases with the addition of liquid paraffin, however, elastic fibers can still be obtained if take-up draw ratio is elevated. Fig 2 shows the relation between elastic recovery after 100% elongation and take-up draw ratio, where draw ratio is calculated approximately from the ratio of the area of the spinneret outlet to that of the fiber cross section. Higher take-up draw ratio is required to obtain elastic fibers with the increase in liquid paraffin content. The curve of cyclic loading is shown in Fig 3, which is typical of hard elastic materials [15,21].

Fig 4 gives the meridional scattering curve of polypropylene fiber containing liquid paraffin. It can be noted that there is a Bragg diffraction peak in the meridional direction for each fiber. In the equatorial direction such diffraction peaks are not observed. This scattering curve is similar to that of hard elastic materials reported [15]. It can be inferred, therefore, that after solid-liquid phase separation in a stress field, the blend of polypropylene with liquid paraffin has a row nucleated structure of stacked lamellae instead of spherulites. *Schematic images such structure have been given in literature[5,21]. Parallel crystal lamellae in polymer are interlinked by noncrystalline chains, and these lamellae are perpendicular to the fiber direction. Liquid paraffin exists in the interlamellar region.*

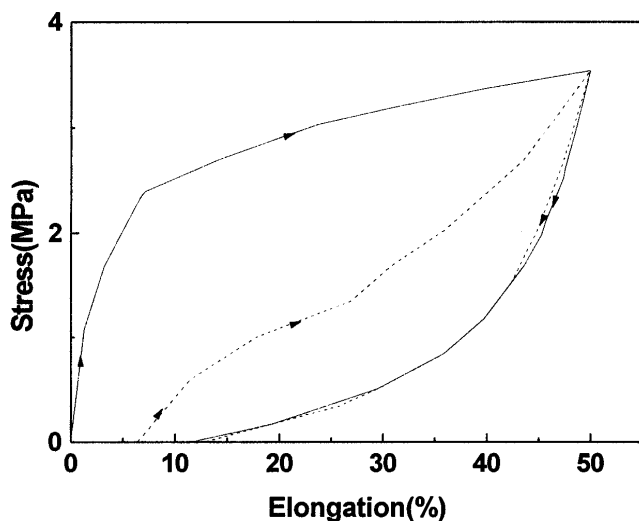


Fig.3 Two cycles loading-unloading curve of PP fiber with 40% liquid paraffin (take-up draw ratio:960, liquid paraffin —first cycle ----second cycle)

The stress-strain curve of fibers with different paraffin contents is shown in Fig 5. With the increase of paraffin content, the yield point decreases considerably. It can be inferred that after the solid-liquid phase separation of liquid paraffin and polypropylene in the stress field, liquid paraffin exists in the polypropylene interlamellar region. We might conceive that polypropylene lamellae are serially interlinked by liquid paraffin in the noncrystalline region in the fiber.

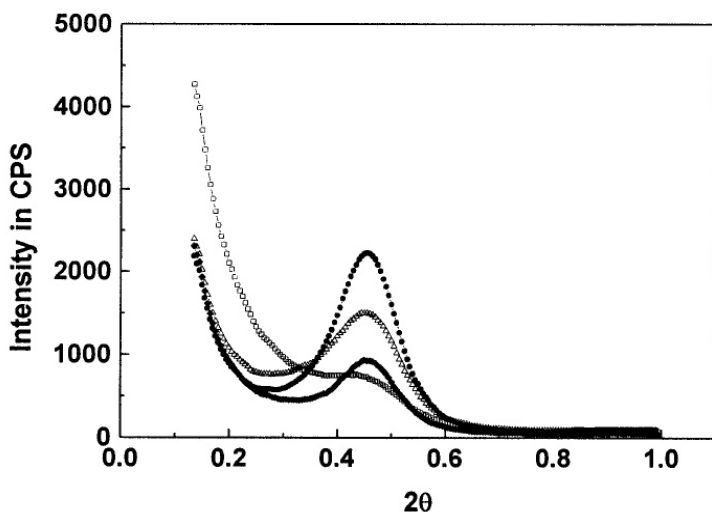


Fig.4 SAXS curve of PP/liquid paraffin fiber (meridional) (take-up draw ratio: 960, liquid paraffin content: (•)10% (Δ)20% (◆)30% (□)40%)

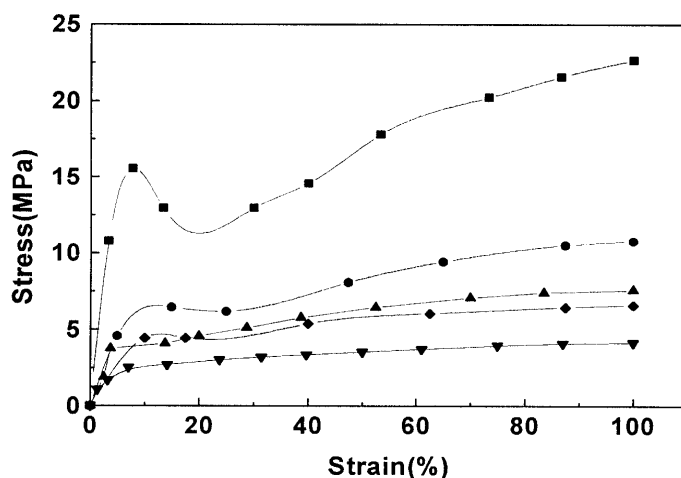


Fig.5 Stress-strain curve of PP fiber with different liquid paraffin contents (take-up draw ratio; 960, liquid paraffin content : (■):0 (●):10% (▲):20% (◆):30% (▼):40%)

Compared with the membrane prepared from hard-elastic polypropylene, micropores in membranes prepared from static TIPS are more tortuous, which lowers permeability of the membrane. With the hard-elastic polypropylene fiber containing liquid paraffin, interaction between lamellae is weakened and lamellae are easier to be separated after the extraction of liquid paraffin in the elastic fiber by solvent. Microporous membranes with high gas permeability were obtained after 40% extension. The properties of such membranes are given in Table 1. *The gas permeability is comparable with data of microporous polypropylene membranes reported in literature[17,22].*

Table 1 Properties of membranes

Nitrogen permeability coefficient ($10^{-5}\text{cm}^3(\text{STP}) \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$)	Bubble point pressure (MPa)	Porosity (%)	Inner diameter(mm)	Wall thickness(mm)
3.4	0.051	42	0.26	0.03

In conclusion, polypropylene fibers containing liquid paraffin spun under high take-up draw ratio have row-nucleated structure of stacked lamellae after solid-liquid phase separation in stress field. Microporous membranes can be obtained by stretching such fibers.

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