Self-Reinforcement of Polypropylene by Flow-Induced Crystallization During Continuous Extrusion

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ABSTRACT: Self-reinforced polypropylene (PP) sheets have been prepared from melt flow-induced crystallization through a conical slit die fed by a conventional extruder. Their structure and properties, influenced by the die pressure ranging from 20 to 50 MPa and die outlet temperature, are studied by scanning electron microscopy observation, differential scanning calorimetry analyses, tensile strength, and light transmittance measurements. At a die outlet temperature of 162°C and a pressure above 30 MPa, conspicuous increases in the melting peak, tensile strength, and light transmittance (they can be used to characterize the self-reinforcement degree of sheet) are observed. The self-reinforcement degree, however, increases only slightly with increasing pressure as it exceeds 40 MPa. Raising the die outlet temperature from 162 to 172°C results in a further increase in the self-reinforcement degree (for example, a highest tensile strength of 288 MPa) while keeping the pressure at 40 MPa, so bulk PP materials with high properties can be produced from continuous melt extrusion under pressures lower than 40 MPa. Furthermore, the melt temperature plays an important role in determining the properties of self-reinforced polymeric materials. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 2111–2118, 1998

Key words: polypropylene; self-reinforcement; extrusion; structure and properties

INTRODUCTION

Self-reinforcement of flexible-chain polymers, such as polyethylene and polypropylene (PP), during extrusion can be achieved by the following two routes: solid-state deformation and melt deformation.[1] In the latter, the high property parts are produced by inducing oriented crystallization in flowing polymer melt. The melt orientation is induced from the extensional flow, and the induced extended-chain crystallization is retained by exactly controlled cooling under a higher pressure.

The flow-induced crystallization takes place in an extremely narrow temperature region, and so the melt temperature within the crystallization area must be controlled with high precision.[2] Perhaps, just for that reason, most of the research work on the self-reinforcement of polyolefins by the melt deformation has mainly concentrated on the discontinuous process carried out with a capillary viscometer fitted with a convergent die,[3–5] with which the enhanced properties were achieved only for thin filaments. The bulk self-reinforced polymeric materials can be produced continuously by melt flow-induced crystallization using conventional extrusion equipment, so this method is of greater practical utility. Unfortunately, only a few studies have been concerned with it.[1,6,7] McHugh et al. prepared self-reinforced PP sheets 2-mm thick with 72.7–112.1 MPa ten-

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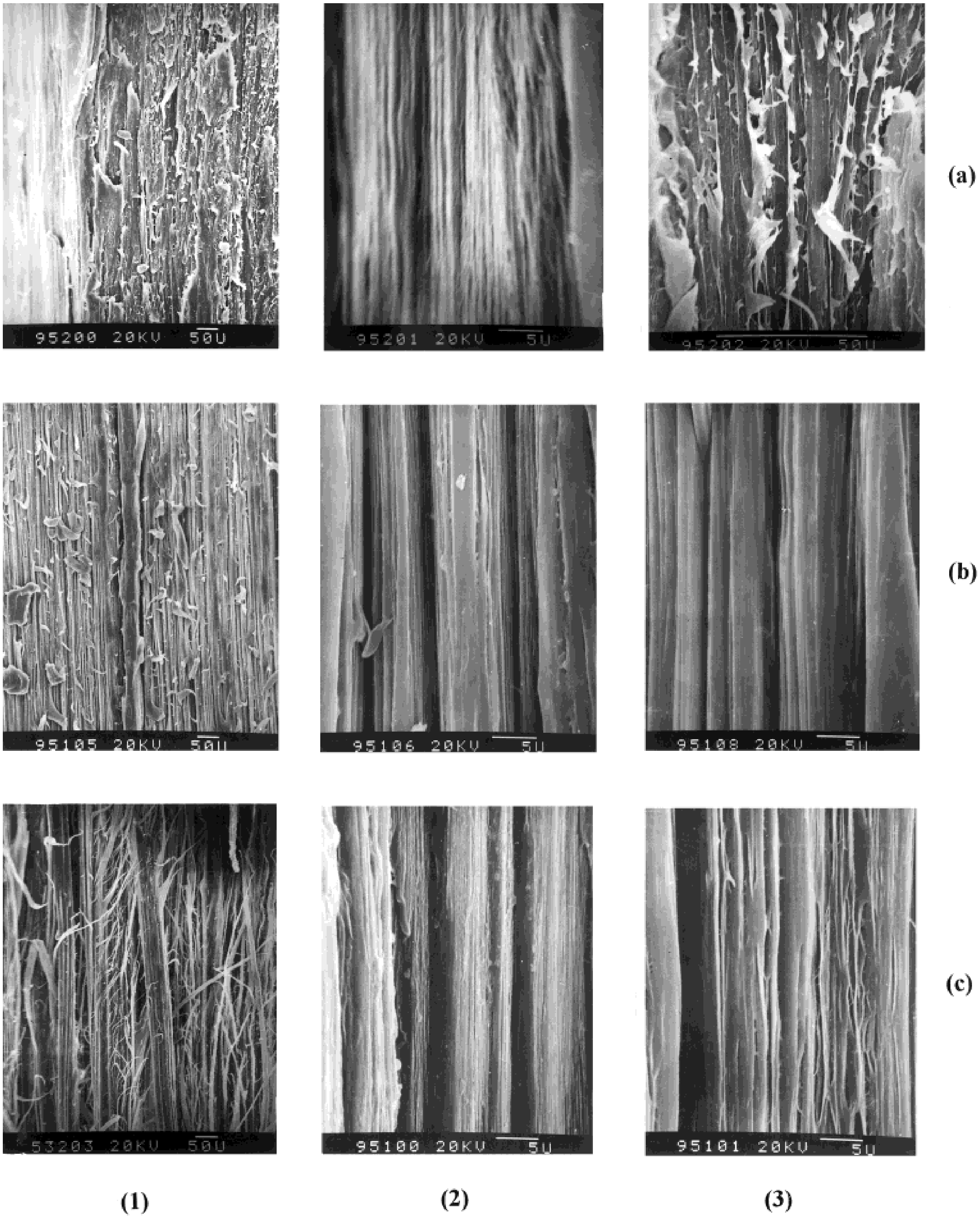

Figure 1 Scanning electron micrographs of the self-reinforced sheets prepared at various die pressures (MPa)/die outlet temperatures (°C), as follows: (a) 20/164; (b) 30/162; (c) 50/162. Orientations are as follows: (1) left is near the outer layer, and right is near the inner core; (2) near the outer layer; (3) near the inner core. The extrusion direction is vertical.

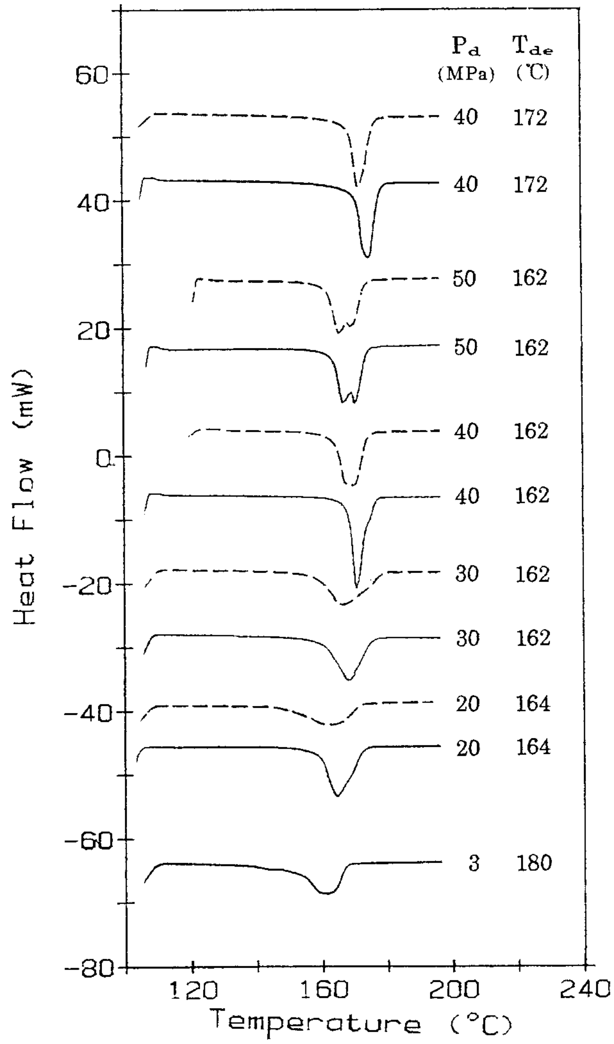

Figure 2 DSC curves of the sheets prepared at various die pressures (P_d) and die outlet temperatures (T_{de}). For the self-reinforced sheets, the solid and dashed lines present the DSC curves of the outer layer and inner core, respectively.

sile strength under an 80 MPa extrusion pressure through flow-induced crystallization during extrusion.[6]

In a previous article by the author,[7] preliminary investigation on the self-reinforced PP sheets prepared from melt flow-induced crystallization during continuous extrusion was carried out. The present article aims to study in detail the influences of the die pressure and die outlet temperature on the structure and properties of the self-reinforced PP sheets prepared from the method above by the scanning electron microscopy (SEM) observation, differential scanning calorimetry (DSC) analyses, and tensile strength and light transmittance measurements.

EXPERIMENTAL

Process Description

The experimental apparatus consists of a 20-mm conventional single-screw extruder with a length-to-diameter ratio of 25/1 and a conical slit die with a tapered entrance semiangle of 30° and width and height at the lip of 20 × 1.5 mm. Three separately heated zones were used for controlling the temperature of the die. The die pressure was measured by a pressure transducer at the die inlet.

A commercially available PP-grade Moplen-RO (Montedison S.P.A., Italy) was used in the present experiments. Its melt flow index (230°C/2.16 kg) was about 8.1 g/10 min.

The normal sheets were prepared at a die outlet temperature of 180°C with a die pressure of about 3 MPa. When preparing the self-reinforced sheets, the die lip was cooled with air jets from a blower in order to lower the die outlet temperature and, hence, to increase the die pressure. Pressures of 20 and 25 MPa were obtained while setting the die outlet temperature at 164°C. To achieve pressures between 30 and 50 MPa, the temperature was lowered to 162°C. After reaching steady-state extrusion at a 162°C temperature and a 40 MPa pressure, the temperature was gradually increased to 172°C while keeping the pressure at 40 MPa, then the specimens were prepared to investigate the influence of the die outlet temperature on their properties.

Test Procedures

The cleaved or torn surfaces of the self-reinforced sheets parallel to their extrusion direction were coated with a gold layer in an Eiko IB3 ion coater and then observed in a Hitachi S-550 SEM microscope.

The DSC measurements were conducted with slices (about 50 μm thick) cut from the specimens on a DuPont DSC Model 1090 unit. For the self-reinforced sheets, the slices were cut parallel to their extrusion direction from the outer layer and inner core, respectively. The heating rate was 10°C per min.

The dumbbell samples were punched from the

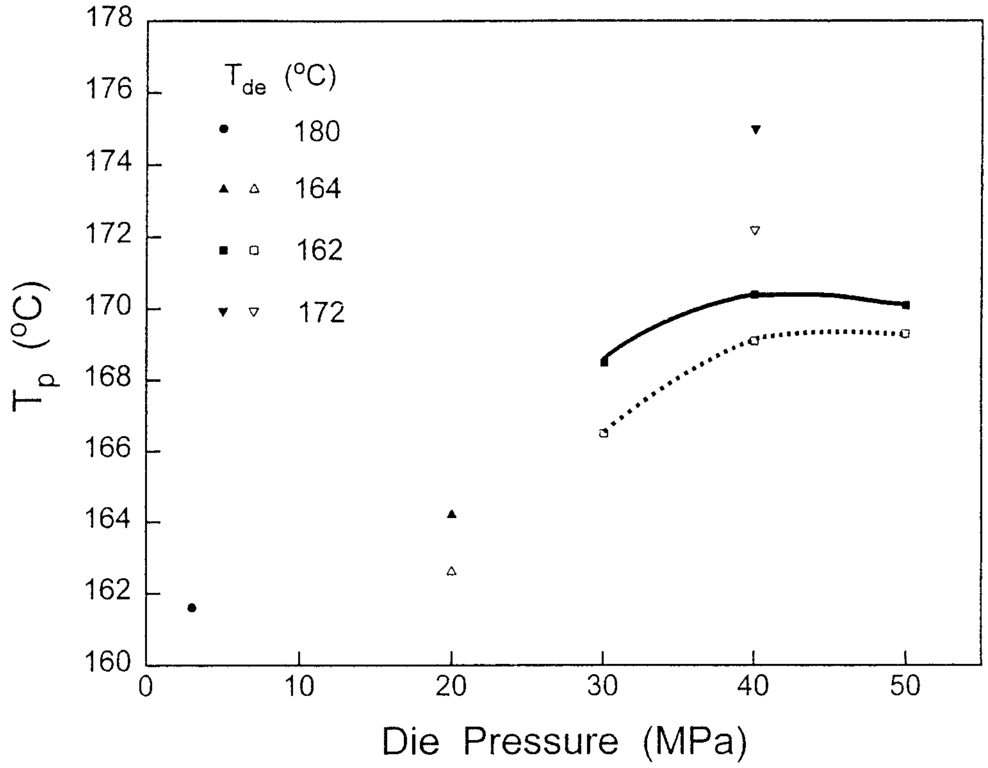

Figure 3 DSC melting peak temperature (T_p) of the sheets as a function of die pressure at four die outlet temperatures (T_{de}). For the self-reinforced sheets, the solid and hollow symbols present the T_p of the outer layer and inner core, respectively.

sheets to measure the tensile strength along their extrusion direction. A Monsanto tensiometer (Model 10) was employed. The measurements were carried out at 23°C and a crosshead speed of 50 mm/min.

The light transmittance of 1.5-mm thick sheets was measured by a spectrophotometer (Model 721) manufactured by Shanghai No. 3 Analyses Instrument Plant. The wavelength of light chosen was 580 nm.

RESULTS

Morphology

The normal PP specimen has a typical spherulite structure consisting of randomly arranged lamellae.[7] Figure 1 shows the electron micrographs of the self-reinforced PP sheets prepared under die pressures of 20, 30, and 50 MPa, respectively. For the self-reinforced sheet prepared at a die outlet temperature of 164°C and a pressure of 20 MPa, fibrous crystalline morphology is formed at the thin outer layer but almost absent over a large inner region [Fig. 1(a)]. The morphology throughout the thickness of the sheets prepared at a die outlet temperature of 162°C and pressures of 30 and 50 MPa, respectively, is fibrous [Fig. 1(b) and (c)]. In particular, the fibrillation is very conspicuous for the latter [Fig. 1(c)].

It seems evident from Figure 1 that the microfibrils extend straight along the extrusion direction and some amorphous regions are embedded between them in the self-reinforced specimens.

Differential Scanning Calorimetry

Shown in Figure 2 are the DSC curves of the slices cut from the sheets prepared at various die pressures and four die outlet temperatures. The correspondent melting peak temperatures are given in Figure 3.

The DSC melting peak of the normal specimen shows a value of 161.6°C. Compared with the normal sheet, the self-reinforced sheet prepared at a

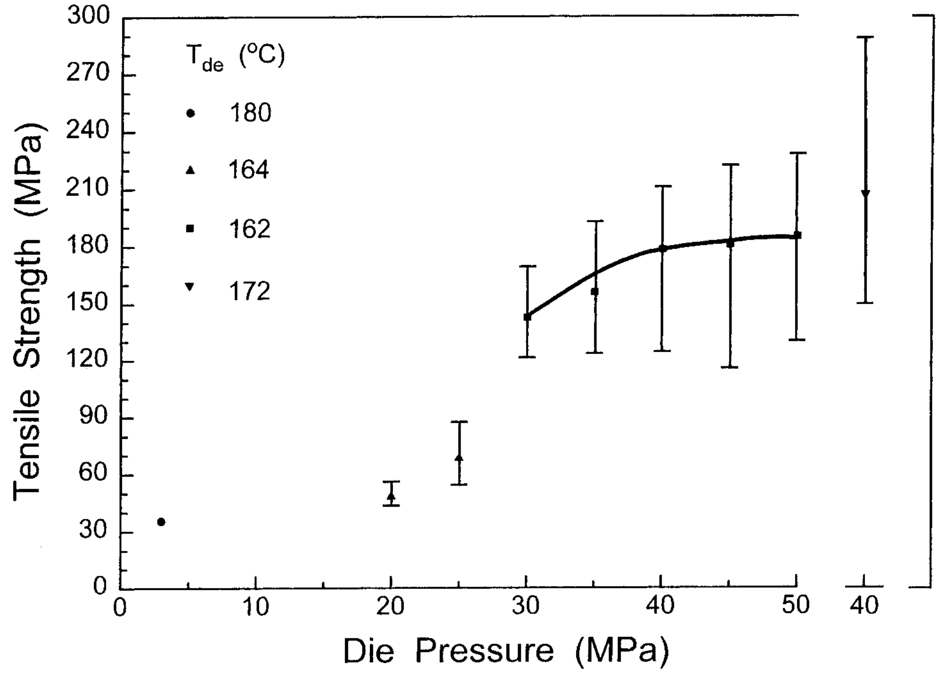

Figure 4 Dependence of the tensile strength of the sheets on the die pressure for different die outlet temperatures (T_{de}).

164°C die outlet temperature and a 20 MPa pressure has a small elevation of melting peak. When the die outlet temperature is set at 162°C and pressure exceeds 30 MPa, the melting peak temperatures of sheets (especially their outer layers) exhibit greater increases. Under a 40 MPa pressure, the melting peak of the sheet is 170.4 and 169.1°C for its outer layer and inner core, respectively. The sheet prepared under a pressure of 50 MPa has a close melting peak with that under 40 MPa. When the die pressure is maintained equal to 40 MPa, an even higher melting peak, which is 175.1°C for the outer layer and 172.2°C for the inner core, is obtained after raising the die outlet temperature from 162 to 172°C, that is, a 13.5 and 10.6°C elevation, respectively, compared to the normal specimen.

As can be clearly seen from Figure 2, the self-reinforced sheets prepared at die pressures of 40 and 50 MPa exhibit an obvious narrower peak shape than the normal sheet. In addition, two distinct melting peaks are observed in the sheet prepared under a 50 MPa pressure. The melting peak for that sheet shown in Figure 3 is its higher one.

Tensile Strength

Figure 4 presents the tensile strength of the sheets as a function of the die pressure at four die outlet temperatures. It is seen that the tensile strength of the self-reinforced sheets has some increase under die pressures of 20 and 25 MPa and a conspicuous increase under pressures higher than 30 MPa at die outlet temperatures used in the experiments presented here. At a die outlet temperature of 162°C, a highest tensile strength of 211 MPa and an average strength of 178.3 MPa are obtained under a 40 MPa pressure. That highest tensile strength is increased by 4.9 times compared to the 35.5 MPa strength of the normal sheet. The tensile strength increases only slightly with further increasing pressure. While fixing the die pressure at 40 MPa, increasing the die outlet temperature from 162 to 172°C results in a further increase in the tensile strength, which is a maximum of 288 MPa, being 8.1 times of that for the normal sheet, and an average of 207 MPa.

It is thus that the highest tensile strength of the self-reinforced PP sheets prepared in this study is not only much higher than that of the glass-reinforced PP or some engineering plastics, but also higher than that of some liquid crystalline polymers.

Light Transmittance

Figure 5 is the photograph of the normal and self-reinforced sheets with a thickness of 1.5 mm. Evi-

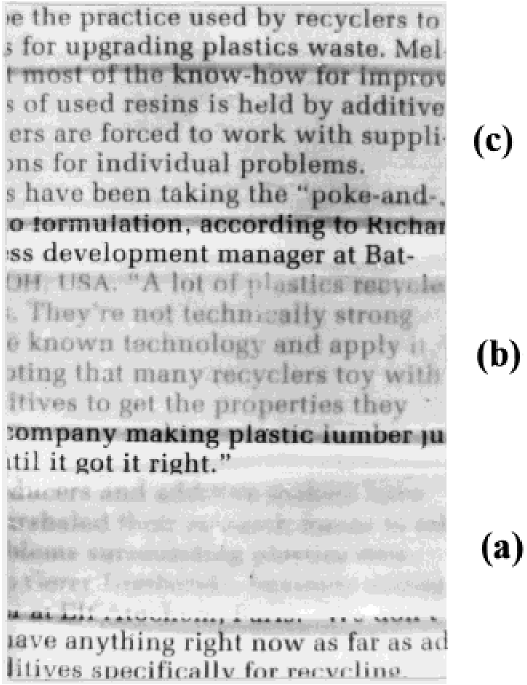

Figure 5 Comparison of the transparency for the sheets 1.5 mm thick prepared at various die pressures (MPa): (a) 3; (b) 20; (c) 40.

dently, the latter is more transparent than the former.

The dependence of the average light transmittance of 1.5-mm thick sheets on the die pressure for four die outlet temperatures is illustrated in Figure 6. It can be seen that the tendency in the light transmittance with respect to the pressure is similar to that observed for the tensile strength. The average light transmittance for the normal sheet is measured to be 29.6%, whereas for the self-reinforced sheets, it increases from 52.8% (a 78.4% increase compared to the normal sheet) at a 162°C die outlet temperature to 57.5% (a 94.3% increase) at 172°C while maintaining the die pressure at 40 MPa.

DISCUSSION

Influence of the Die Pressure on the Structure and Properties of Self-Reinforced Sheets

From Figure 1, it is evident that the macroscopic structure throughout the thickness of the self-reinforced PP sheets prepared under die pressures above 30 MPa exhibits a fibrous morphology. The results of DSC analyses and tensile strength and light transmittance measurements (shown in Figs. 2–4 and 6) reveal quantitatively the influence of the die pressure on the structure and properties of the self-reinforced sheets. There are pronounced increases in the melting peak temperature, tensile strength, and light transmittance for the sheets prepared at a die outlet temperature of 162°C and beyond a pressure of 30 MPa. The latter two parameters, however, increase only slightly with increasing pressure with it in excess of 40 MPa.

Two things account for the preceding occurrence. First, the crystallite melting point of the polymer is raised with the aid of the increased pressure. A 162°C die outlet temperature used in this study is close to the equilibrium crystalline melting point of PP. Higher die pressures increase the viscosity of the PP melt in the convergent channel (especially near its walls) of the die and, hence, retards melt flow, which leads to the reduction of molecular mobility and deformation rate of the melt. Concomitantly, the formation of oriented extended-chains of molecules is hindered to some extent. In fact, it has been found in this experimental process that the extrusion line speed of the sheet was slightly lower at a 50 MPa die pressure than at a lower one (for example, 40 MPa) with the die outlet temperature kept at 162°C. Secondly, the disruptive influence of the shear flow could destroy some of the molecular orientation obtained by the extensional flow at a higher pressure and lower melt temperature, which has been noted by Ghosh et al.[8]

From the foregoing, it is demonstrated that the dependence of the melting peak temperature, tensile strength, and light transmittance on the die pressure is similar for the self-reinforced sheets. In other words, the self-reinforced sheets with higher clarity have a higher temperature resistant crystalline structure and tensile strength at the same time. This is because of the fact that the factor affecting those three parameters (they can be used to characterize the self-reinforcement degree of the sheet) is the same, which is the orientational degree of molecular chains in polymers. The ideal die pressure is about 40 MPa for the die outlet temperatures used in the present study. Thus, the bulk PP materials with high properties can be produced from flow-induced crystallization during continuous melt extrusion at an extrusion pressure of 40 MPa or lower, which is much lower than that reported in the references.[1,6] This can be briefly explained in terms of the thermodynam-

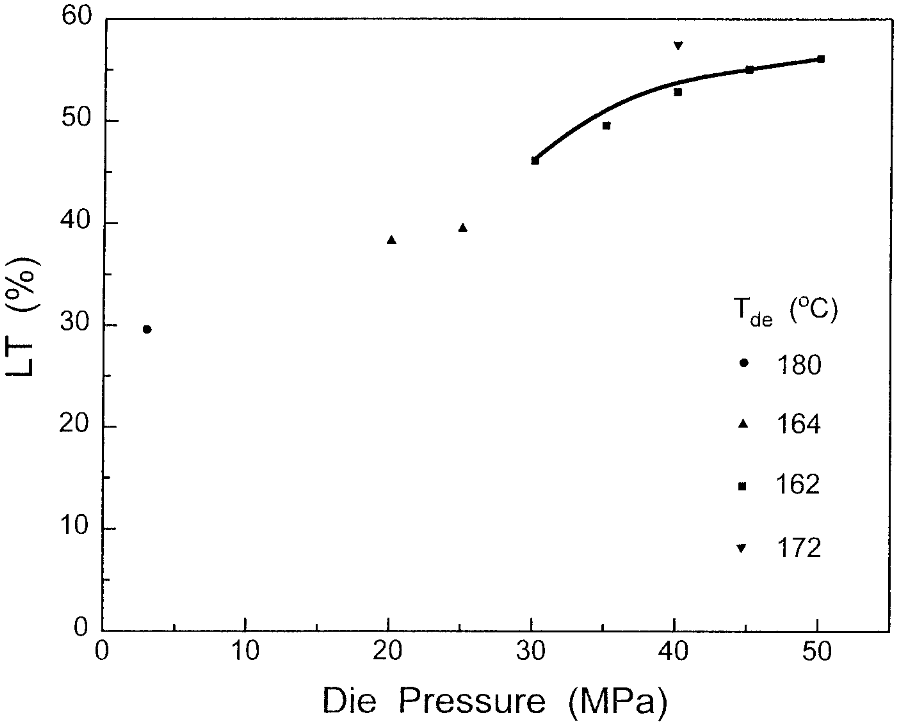

Figure 6 Influence of the die pressure on the average light transmittance (LT) of the sheets 1.5 mm thick at different die outlet temperatures (T_{de}).

ics in conjunction with the flow field of a polymer melt flowing through a wedge-shaped convergent channel as follows.

The change in Gibbs free energy in a system undergoing change in state is defined by

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

where ΔG is the change in Gibbs free energy, ΔH is the enthalpy change, T is the absolute temperature, and ΔS is the entropy change.

Referring to the analyses made by Collier et al.,[9] ΔG can be expressed as follow

$$\Delta G \propto \dot{\varepsilon} \tag{2}$$

where $\dot{\varepsilon}$ is the extensional strain rate of the polymer melt along the flow direction.

With the method of the direct visual observation in conjunction with the theoretical analysis, the author revealed the distribution regularity of the velocity and $\dot{\varepsilon}$ of a polymer melt flowing through a wedge-shaped convergent channel.[10] The experimental apparatus was composed of a conventional extruder, a specially designed conical slit die fitted with optical glass windows, and a video capture system. It has been demonstrated that along the flow direction, $\dot{\varepsilon}$ increases slowly at first and abruptly within a narrow region as approaching the exit of the convergent channel, reaching a maximum at the exit. At the exit, it is several orders of magnitude greater than that at the entrance, depending on the cross-sectional area reduction ratio in the convergent channel. From eq. (2), a higher $\dot{\varepsilon}$ can cause the free energy change upon crystallization (that is, the thermodynamic driving force for crystallization) of flowing polymer melt to increase. In addition, a higher $\dot{\varepsilon}$ can cause the molecular chains of the polymer to be extended and to develop parallel alignment more easily and, hence, reduce dramatically the major resistance to crystallization. Increasing the driving force for crystallization and decreasing the resistance can lead the flowing polymer melt to crystallize at a high rate. In the die used for preparing the self-reinforced specimens, the convergent channel is followed by the straight channel with a constant cross-sectional area. Obviously, the level of molecular orientation is very low in the shear flow region of the straight channel. So, the extended-chains would be most apt to crystallize within a narrow area just preceding the entrance to the straight channel. The foregoing analyses clearly indicate that achieving the crystallization of molecular chains subjected to the highest orientation within that narrow area by carefully controlling the die temperature may favor to extrude the bulk polymeric materials with high performance from melt under a continuous condition with a lower pressure (for example, 40 MPa or lower).

Influence of the Die Outlet Temperature on the Structure and Properties of Self-Reinforced Sheets

Under steady-state extrusion conditions at a die outlet temperature of 162°C and a die pressure of 40 MPa, the former was gradually raised to 172°C with the latter maintained at 40 MPa. The self-reinforced sheet prepared at 172°C temperature exhibits a higher value in the melting peak temperature (Figs. 2 and 3), tensile strength (Fig. 4), and light transmittance (Fig. 6) and, hence, a more highly oriented extended-chain crystalline structure than at 162°C. This can be contributed to two facts that occur as the die outlet temperature appropriately increases. The one is that the molecular mobility and deformation rate of the polymer melt subjected to a higher pressure in the convergent channel of the die are improved, which promotes the formation of oriented extended-chains of molecules. It has been found in this experimental procedure that with increasing the die outlet temperature from 162 to 172°C, the screw speed of the extruder was required to be raised to maintain a 40 MPa die pressure, and, at the same time, the extrusion line speed of the sheet increased to some extent. The other is that the previously mentioned disruptive influence of the shear flow on the molecular orientation could be weakened.

However, the die outlet could not be set at a too high a temperature. Otherwise, extended-chains in the polymer formed in the convergent channel will tend to relax in the following straight channel of the die. The ideal would be to localize the crystallization just in front of the entrance to the straight channel where the highest extensional strain rate occurs, by exactly controlling the die outlet temperature in conjunction with maintaining a temperature gradient between the inlet and outlet of the die.

CONCLUSIONS

The self-reinforced PP sheets, 1.5 mm thick, were prepared by melt flow-induced crystallization using a conventional extruder and a conical slit die. Their structure and properties influenced by the die pressure and die outlet temperature are investigated in detail by the SEM observation, DSC analyses, and tensile strength and light transmittance measurements. The die pressure varies from 20 to 50 MPa, whereas the die outlet temperatures used are 162, 164, and 172°C, respectively. It has been demonstrated that the bulk PP materials with high properties can be produced from continuous melt extrusion under extrusion pressures lower than 40 MPa. Moreover, control of the melt temperature is very important for generating the properties of self-reinforced polymeric materials.

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