EFFECT OF MELT TEMPERATURE ON THE PHASE MORPHOLOGY, THERMAL BEHAVIOR AND MECHANICAL PROPERTIES OF INJECTION-MOLDED PP/LLDPE BLENDS[*]

Run Su, Ke Wang, Qin Zhang[**], Feng Chen and Qiang Fu[**]

Department of Polymer Science & Materials, Sichuan University, State Key Laboratory of Polymer Materials Engineering, Chengdu 610065, China

Abstract   The phase morphology and thermal behavior of various isotactic polypropylene (PP)/linear low density polyethylene (LLDPE) blends were investigated with aid of scanning electron microscopy (SEM) and differential scanning calorimetry (DSC), respectively. The effect of barrel (melt) temperature on the morphology, thermal behavior and the resultant mechanical properties of the injection molded bars was the research focus, and the influence of LLDPE composition was also taken into account. It was found that the mechanical properties, especially the tensile ductility and the impact strength, were greatly affected by the processing temperature. The samples obtained at low temperatures had the highest elongation at break and impact strength, while those molded at high temperatures had the poorest toughness. Two reasons were responsible for that: first, the phase size in the samples increased with the processing temperature; second, possible orientation existed in the samples obtained at low processing temperatures.

Keywords: Injection molding; Polypropylene; LLDPE; Morphology; Orientation; Mechanical properties.

INTRODUCTION

Multiphase polymer blends usually have their mechanical properties strongly affected by the size and morphology of the phases, the crystalline structure as well as crystallinity generated during its processing. So the processing conditions, such as mixing speed[1–3], mixing time[4–6] and temperature[2–4, 7–9], will greatly influence the structures of polymer blends and thus the mechanical properties. Temperature is one of the most important processing variables, which can determine the phase morphology and crystalline structure to a great extent. Many researchers reported the effect of processing temperature on the phase morphologies of different polymer blends. For a co-continuous structure, temperature induced coalescence (coarsening)[10], change of continuity degree[7] and stability[11] were the concerns. Crystalline structure was also controllable by designing suitable temperatures during processing[9]. For injection molding, the temperatures should be drawn close attention included barrel temperature[8, 12] and mold temperature[12, 13]. The variation of the two temperatures would greatly influence the phase and crystalline morphologies and resultant mechanical behavior.

Polyolefins are the most important plastics. Polyethylene and polypropylene are the biggest products, and lie in the first position of plastics. Blends of different polyolefins are frequently used to get the balanced mechanical and processing properties. For example, LLDPE/LDPE blends have properties which combine the

high toughness of LLDPE and the good melt processability of LDPE. The properties of an individual polyolefin can be changed in a significant way by mixing with other component. For this reason, polyolefin blends have obtained widespread commercial applications[14–16]. It has been a long-standing interest for polymer researchers to understand the relationships between morphology and properties of polyolefin blends, and to control the micro-phase separation, morphology and orientation of studied blends, in order to obtain excellent properties.

As a part of a long-term project aimed at super polyolefin blends, we are seeking to establish a fundamental understanding of structure-property-processing relationships through controlling phase separation, molecular orientation and crystal morphology of polyolefin blends. In this work, we focused on the effect of melt or barrel temperature on the phase morphology, thermal behavior and the resultant mechanical properties of the polypropylene (PP)/linear low density polyethylene (LLDPE) blend bars, obtained *via* injection molding. The LLDPE content was also taken into account. PP/LLDPE blends in the whole composition range were first prepared by a co-rotating twin-screw extruder, and then were injection molded to dumbbell-shaped bars, with barrel temperature changed. The morphology, melting and crystallization behavior of both PP and LLDPE in the blends were investigated with aid of scanning electron microscopy (SEM) and differential scanning calorimetry (DSC), respectively. Mechanical properties of the PP/LLDPE blends were also investigated in detail with respect to them.

EXPERIMENTAL

Materials
A commercially available LLDPE (trade marked as 7042) with melt flow index (MFI) of 2.0 g/10min (190°C, 2.16 kg), was supplied by Jilin Petrochemical Corp, China. Isotactic polypropylene (*i*PP) T30S was a commercial product of Dushanzi Co. Ltd, China. The MFI of PP was 2.8 g/10min (2.16 kg, 230°C).

Samples Preparation
LLDPE and PP were melt compounded together using a TSSJ-25 co-rotating twin-screw extruder with a barrel temperature of 160–190°C. After pelleting and drying, the blends were fed into an injection-molding machine (PS40E5ASE, Japan) to prepare the specimens. The dumbbell-shaped bars were obtained for structural characterization and mechanical properties testing. The barrel temperature could be changed in our injection-molding machine during the experiment, that was: low temperature (200°C), moderate temperature (220°C) and high temperature (240°C), abbreviated as LT, MT and HT, respectively. The as-obtained samples were labeled according to the temperature and the weight content of LLDPE. For example, HT30 represented the sample was obtained at high barrel temperature (240°C), and the LLDPE content was 30 wt%.

Scanning Electron Microscopy (SEM)
The specimens were first etched chemically by cyclohexane at 85°C for one hour to etch away the LLDPE phase. Then the surface was coated with gold and subsequently examined by an FEI Inspect F scanning electron microscope instrument at 20 kV.

Differential Scanning Calorimetry (DSC)
The thermal analysis of the samples including homopolymers and blends was conducted under nitrogen using a Perkin-Elmer pyris-1 DSC with indium calibration. Two cases in which the thermal history was partially reserved or completely erased were designed. For the case of partially reserving thermal history, the samples were first heated at a rate of 10 K/min to 180°C, held for 2 min, and cooled at −10 K/min to 50°C; For the case of completely erasing the thermal history, the samples were heated to 220°C, held for 10 min, and cooled at −10 K/min to 50°C. The peak crystallization temperature and the onset temperature were calculated by the supplied software.

Mechanical Property Measurements
An SANS universal testing machine (Shenzhen, China) was used to measure the tensile properties, with a

moving speed of 50 mm/min. The measure temperature was 23°C. For impact strength, the notched impact strength was tested with an I200XJU-2.75 Izod impact tester at room temperature. The values of all the mechanical parameters were calculated as averages over six to nine specimens for each composition.

RESULTS AND DISCUSSION

Mechanical Properties

The tensile strength and modulus of various PP/LLDPE blend bars obtained at different barrel temperatures are shown in Fig. 1. One can clearly see that both of the two tensile properties will experience almost a linear decrease with the increase of LLDPE content, due to the characteristics of LLDPE. When referring to the effect of the melt or barrel temperature on the tensile properties, however, there is no obvious regularity, and the tensile strength and modulus keep more or less constant at three temperatures used.
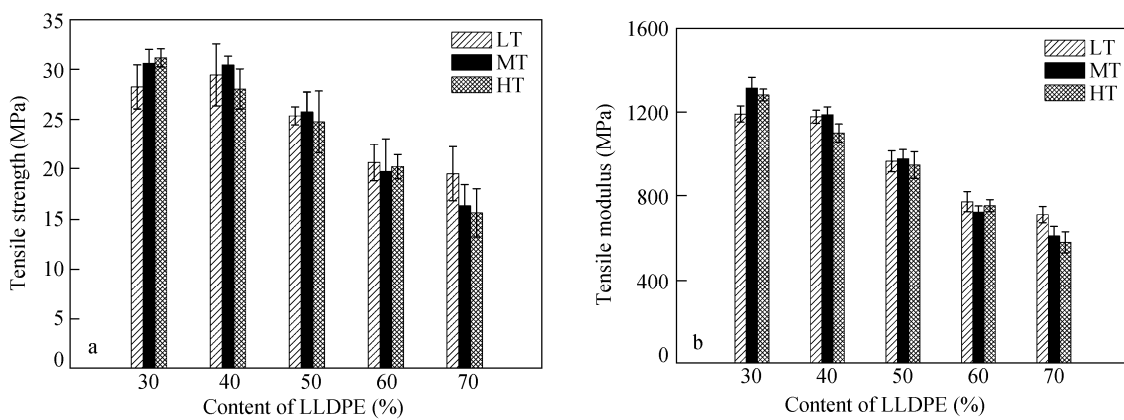

Fig. 1 Tensile strength (a) and modulus (b) for various injection molded bars obtained at different barrel temperatures
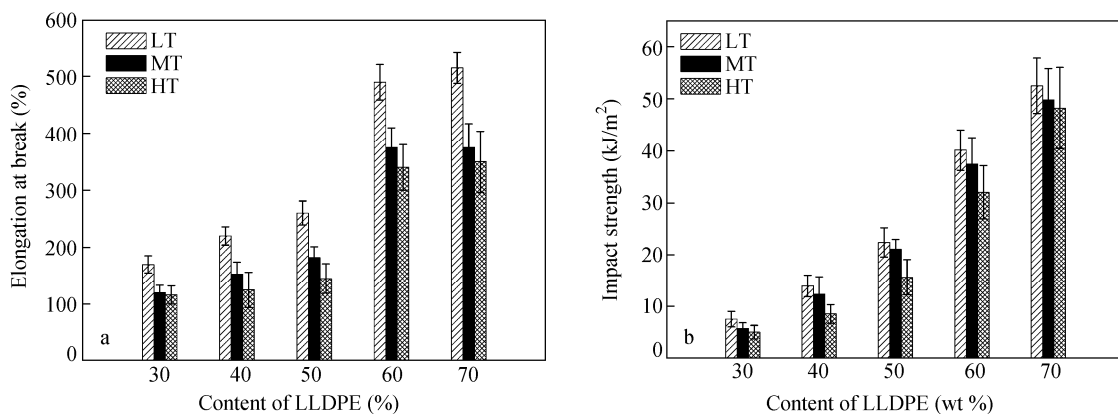

Fig. 2 Elongation at break (a) and impact strength (b) of various injection molded bars obtained at different barrel temperatures

Figure 2 illustrates the elongation at break and impact strength of those injection molded bars, which represent tensile ductility and impact toughness, respectively. Both of the two kinds of toughness are improved with increasing the content of LLDPE component, especially when the LLDPE content is between 60 wt% and 70 wt%. As we know, LLDPE itself is of good toughness. When LLDPE is the matrix, the mechanical properties

of the blend are mainly dependent on those of LLDPE. Interestingly, the samples obtained at low temperature have the highest elongation at break and impact strength, while those obtained at high temperature have the poorest toughness, regardless the content of LLDPE. To understand the relationship between processing temperature and the mechanical properties, the change of phase morphology with respect to temperature should be first investigated.

Phase Morphologies

SEM photographs of samples with 50 wt% LLDPE obtained at different temperatures are shown in Fig. 3. At this concentration of LLDPE a co-continuous structure can be seen. It is clear that the phase sizes of both LLDPE and PP increase substantially (namely coarsening) though the co-continuity has been maintained, which is in accordance with the results of previous literatures[7, 17, 18]. This coarsening effect of co-continuous morphology in polymer blends can be attributed to phase coalescence, which is believed to be favored by the interfacial tension between these immiscible or partially miscible blend components and also by a decrease in the flow viscosity during the molding process at higher temperatures[7].
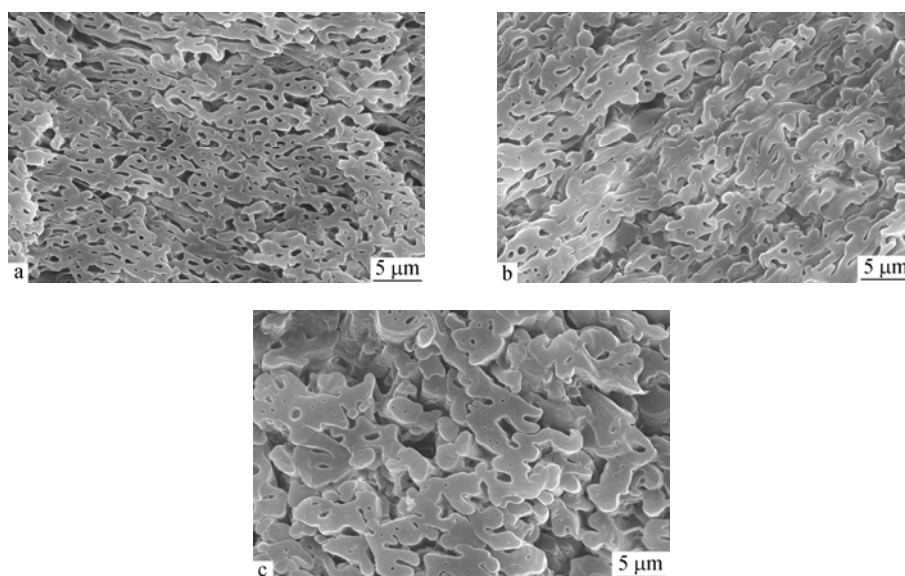

Fig. 3 SEM photographs of samples with 50 wt% LLDPE molded at different temperatures: (a) LT50, (b) MT50 and (c) HT50

To verify the influence of temperature on the phase structure in PP/LLDPE blends, samples with 30 wt% LLDPE obtained at different temperatures are examined, and the result is shown in Fig. 4. Just as the above observations, the domain size of the dispersed phase (LLDPE) increases with the increase of molding temperature, from about 450 nm (LT30) to 1200 nm (HT30). Thus it can be concluded that the processing temperature greatly influences the phase morphology of PP/LLDPE blends, whether for co-continuous or sea-island structure. The higher the temperature is, the larger the phase size will be. It is widely recognized that large domain size will usually result in poor mechanical properties. There are many reports about the relationship between phase (domain) size and the mechanical properties[19–21]. Pang *et al.* hold that the decrease of interphase and a sharper boundary resulting from domain coarsening during the late-stage phase separation were responsible for the poor tensile properties[19].

Thermal Behavior

Since the mechanical properties are also closely related to the orientation reserved in samples after processing, DSC experiments were carried out to detect the possible orientation of samples obtained at different processing

temperatures and to understand the differences of mechanical properties among the samples obtained at different processing temperatures in view of orientation. DSC cooling curves for samples with 50 wt% LLDPE obtained at different barrel temperatures are shown in Fig. 5(a). Noting that it is the first DSC run and the thermal history is not completely eliminated (holding at 180°C for 2 min). The crystallization temperature of PP is enhanced in the blend sample molded at low temperature. To verify that change, the samples with 30 wt% LLDPE obtained at different temperatures are examined, and the DSC cooling curves are shown in Fig. 5(b). One can find that the T_c of PP is increased indeed in the blend obtained at low temperature, though the change is small. This phenomenon suggests that samples obtained at low temperature may have a higher degree of orientation, which can nucleate and crystallize at higher temperature during cooling. It is understandable that low processing temperature is favorable for the fixing of orientation. In most cases, orientation often results in a low break elongation[22, 23]. Nevertheless, a quite lot reports can be also found that orientation can also improve the tensile ductility, especially when the orientation degree is not high[24, 25]. Aoyagi *et al.* believed that high elongation at break was generated by the orientation of amorphous region between crystal regions in a drawn film[25].
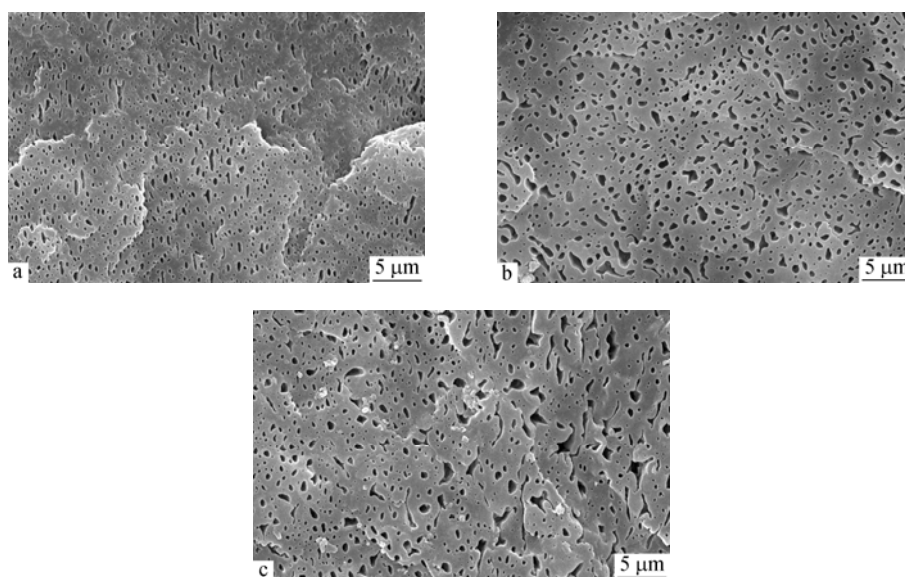

Fig. 4 SEM photographs of samples with 30 wt% LLDPE molded at different temperatures: (a) LT30, (b) MT30 and (c) HT30
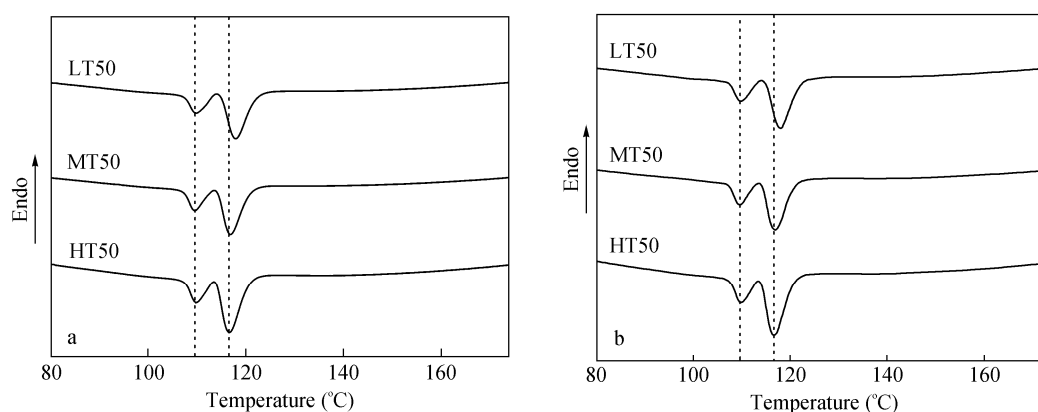

Fig. 5 DSC cooling curves for samples with (a) 50 wt% and (b) 30 wt% LLDPE molded at different temperatures

Sometimes, the orientation of fillers will favor the improvement in ductility[26]. Moreover, it is found that the increment of impact strength could be realized by orientation[27]. Thus, in addition to the small domain size, the possible orientation in the samples obtained at low processing temperature may also contribute to the higher impact strength and larger elongation at break. Of course, the orientation can not be accurately determined by DSC, 2d-WAXD experiments will be carried out in our future work.

Figure 6 shows the DSC heating curves for various samples obtained at moderate temperature (220°C) after erasing the thermal history (holding at 220°C for 10 min). One can see that the melting temperature (T_m) of PP decreases while the T_m of LLDPE increases in the blends compared with that in homopolymers. It indicates a partial miscibility between the two components. Many research works have reported that PP and LLDPE are miscible under certain conditions[28–30]. The partial miscibility can be also demonstrated from the linear change of tensile strength (or modulus) with the content of LLDPE. For immiscible blends, however, the tensile strength will probably decrease first and then increase when changing the composition, and the minimum value corresponds to phase inversion[31–33].
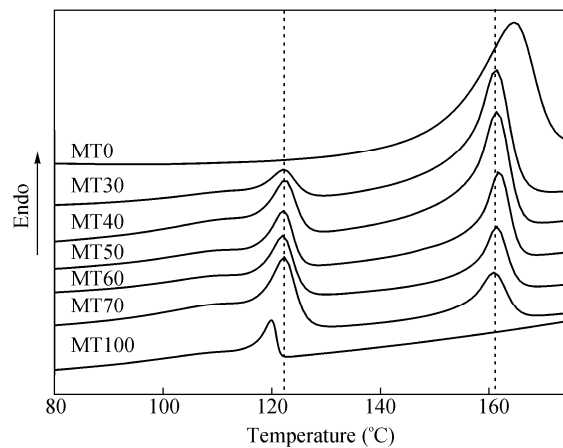

Fig. 6 DSC heating curves for various samples obtained at moderate temperature

As we know, crystallinity also has influence on the mechanical properties of polymer materials. So it is necessary to exam the change of crystallinities of PP and LLDPE in the blends, and the results are shown in Fig. 7. Obviously, the change of LLDPE content or processing temperature has no effect on the crystallinities of the two components. Thus, the main factors which affect the mechanical properties of the blend bars should be the phase size and possible orientation.
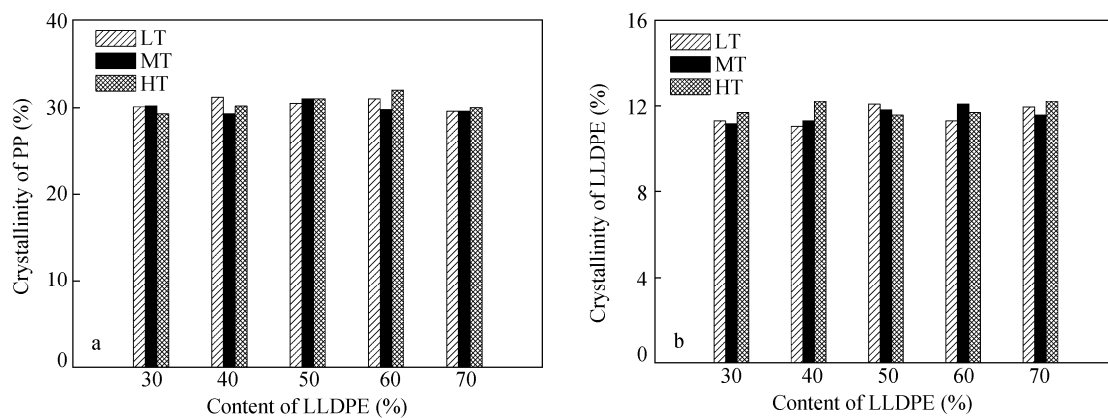

Fig. 7 Crystallinities of PP (a) and LLDPE (b) in various samples obtained at different temperatures

CONCLUTIONS

The effects of processing temperature on the phase morphology, thermal behavior and resultant mechanical properties were investigated for the PP/LLDPE blends. The mechanical properties, especially the tensile ductility and the impact strength, are greatly influenced by processing temperature. The samples obtained at low temperature have the highest elongation at break and impact strength, while those obtained at high temperature have the poorest toughness. There are mainly two reasons for that, first because the phase size increases with the processing temperature; second, possible orientation exists in the samples obtained at low processing temperature.

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