Effect of multiple extrusion on phase structure and properties of impact copolymerized polypropylene

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Abstract: As a typical multi-component polymer, impact polypropylene copolymer (IPC) experiences the phase structure evolution during repeated processing, and the coarsening of phase domain often occurs. In this work, two IPCs with different molecular weight of rubber phase were compared systematically. The evolution of IPC phase morphology and crystallization behavior after multiple extrusion were studied through scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). The materials mechanical properties were tested. Then the influence of rubber phase molecular weight on the phase morphology evolution and the properties after repeated extrusion were discussed in detail. It was found that for the IPC with low molecular weight of rubber phase, the size of rubber phase became smaller and dispersed more evenly with the increase of extrusion times; for the IPC with high molecular weight of rubber phase, the rubber phase size turned to unstable after multiple shearing. The rubber phase size had a complex effect on IPC mechanical properties.

1. Introduction
In the past three decades, impact polypropylene copolymer (IPC) has been widely used in auto industry, electrical appliances and other fields for its excellent mechanical properties (especially at low temperature) and relatively low production cost [1-6]. The typical in-situ copolymerized impact polypropylene is prepared by two-step sequential polymerization process. In the first step propylene homopolymerization is conducted to form polypropylene (HPP) as continuous matrix of IPC; In the second step ethylene/α-olefin copolymerization was carried out to generate rubber phase that dispersed in HPP matrix to improve the impact resistance of the product. Due to the special polymerization procedure and the complex polymer composition, IPC is often named as multi-component multi-phase in-situ alloy [7-10].

As a multi-component and multi-phase polymer material, the macro mechanical properties of IPC are affected by its micro composition structure (molecular composition) and aggregation structure of submicroscopic (phase structure, crystallization behavior) [11-14]. Many scholars revealed that the most important factors affecting the impact resistance of IPC are as follows: (1) the molecular weight, the molecular weight distribution, and the crystallinity of HPP matrix; (2) the molecular weight and ethylene content in rubber phase, and the volume fraction, the dimension and the uniformity of the rubber phase dispersed in HPP; (3) the adhesion and compatibility of HPP matrix and rubber phase.
It was reported that the optimal rubber phase size was related to the temperature. Generally, good mechanical properties occurred at 23°C when the rubber phase particle size was 0.4-0.6 \( \mu m \), at 0°C when the rubber phase was 0.8-1 \( \mu m \), and at -40°C when the rubber phase was 1.2-1.5 \( \mu m \) \cite{16, 18}. Once the rubber and HPP matrix are determined, rubber phase size is the most important factor affecting the toughening efficiency. Wu et al. \cite{19-21} studied the effects of rubber size and rubber-matrix adhesion on notched impact toughness of nylon/rubber blends, revealing a sharp brittle-tough transition occurring at a critical rubber size and proposing a quantitative formula to depict the correlation between the critical dimension of rubber particle and the critical matrix-ligament thickness.

Generally, IPC products undergo at least three extrusion processes before reaching their final application. The first extrusion is the granulation process after the polymerization to add additives such as antioxidants. The second extrusion is the modification process, in which by further adding polyolefin elastomer (POE), talcum powder and other components during the extrusion process to improve the final performance of the products \cite{22-24}. The third extrusion is the injection of the above modified IPC material into the actual mold to form the final product. However, as one of the typical multi-component polymers, the phase structure of IPC is unstable during processing, and the coarsening of phase domain may occur \cite{13, 16}. Therefore, it is necessary to study the change of phase size and phase dispersion of IPC after multiple extrusion, and finally establish the relationship between the micro phase structure and the macro mechanical properties of IPC products. In this work, the phase morphology, crystallization behavior and mechanical properties of two kinds of IPC samples (EP533N1-1 and EP533N2-1 with different molecular weights of rubber phase) after two and three times extrusion processes were studied systematically, to provide guidance for the selection of IPC raw materials in different application fields.

### 2. Experimental section

#### 2.1. Materials

Two commercial IPC granular products (EP533N1-1, EP533N2-1) were produced by Lanzhou Petrochemical Co. of China. By solvent classification method, IPC were first completely dissolved in boiling \( o \)-xylene at 145°C for 30min and then cooled down to 25°C isolate the solution and insoluble substance. The specific operation procedure was detailed before. \( o \)-Xylene soluble substance at 25°C can be considered as rubber phase (EPR). \( o \)-xylene insoluble substance at 25°C can be considered as homo-polypropylene (HPP). The intrinsic viscosity and viscosity average molecular weight of EPR and HPP were measured by viscosity method, and the test temperature was 135°C with decalin as solvent, when calculating viscosity average molecular weight, \( K=1.10 \times 10^{-4} \), \( \alpha=0.8 \). The detailed characteristics are listed in Table 1.

| Sample    | Ethylene content, wt% | Rubber phase content, wt% | \( [\eta]_{\text{EPR}}, \text{dL/g} \) | \( M_{\eta,\text{EPR}}, 10^5 \text{g/mol} \) | \( [\eta]_{\text{HPP}}, \text{dL/g} \) | \( M_{\eta,\text{HPP}}, 10^5 \text{g/mol} \) |
|-----------|-----------------------|---------------------------|-----------------------------------|-------------------------------------|-----------------------------------|-----------------------------------|
| EP533N1-1 | 10.1                  | 20.2                      | 3.694                             | 4.55                                | 1.482                             | 1.45                              |
| EP533N2-1 | 8.7                   | 15.7                      | 5.201                             | 6.97                                | 1.537                             | 1.52                              |

The IPC pellets were extrusioned in twin screw extruder (ZSE-34, Leistrisize, Germany) under same designated extrusion conditions (extrusion temperature 190°C, main machine speed of extruder granulator 120 rpm, feeder speed 20 rpm) with adding a small amount of antioxidant (antioxidant 1010, 0.04 wt% per extrusion; antioxidant 168, 0.08 wt% per extrusion). Each IPC was extruded twice. The secondary and tertiary extrusion samples are named as EP533N1-2, EP533N1-3 for EP533N1-1 product. The secondary and tertiary extrusion samples are named as EP533N2-2, EP533N2-3 for EP533N2-1 product. Finally, the Charpy impact strength and Flexural modulus specimens with the size 80mm×10mm×4mm were prepared by injection molding at 190°C under 25 MPa (injection
pressure and holding pressure) and the molding cycle was 1 min.

2.2 Molecular weight and molecular weight distribution
In order to investigate the degradation or cross-linking of IPC samples after multiple extrusion. The molecular weight and molecular weight distribution of multiple extrusion IPC pellets were examined by high-temperature gel permeation chromatography (GPC) (GPC-IR Polymer Char Co.) at 160°C and using 1,2,4-trichloro-benzene as solvent.

2.3 Scanning electron microscope (SEM) observation
Injection molding IPC specimens were quickly quenched after cooling in liquid nitrogen. In order to clarify the complex phase structure, the samples quenching sections were adequately etched in n-heptane at 23°C for 96 h in ultrasound instrument, then drying in an oven for 1 hour at 80°C. After, the quenching sections of these samples were all sputter-coated with gold powder were observed by SEM (ULTR Aplus Scanning Electron Microscope Produced by Carl Zeiss, Germany)

2.4 Differential scanning calorimetry (DSC)
The thermal behavior of multiple extrusion samples were examined by using a differential scanning calorimetry (DSC 214 Polyma, manufactured by NetZSCH Germany) with nitrogen as purge gas. Per sample was taken about 6 mg and was sealed in an aluminum foil crucible. The samples were first heated to 200°C and held for 5 min to eliminate thermal history, and then cooled down to 30°C and maintained for 5 min. Finally, the samples were heated to 200°C again. The second heating curve and the first crystallization curve are recorded. Both the heating and cooling rates were 10°C/min.

2.5 Mechanical properties
The notched charpy impact strength is tested by XJU-5.5 impact tester produced by Chengde Jinjian Testing Instrument Company in china according to ISO 179-1:2000. Melt flow rate (MFR) was tested by PXRZ-400C melt flow rate meter produced by Ceast Company in Italy according to ISO 1133:1997. The flexural modulus was measured following ISO 178:1993 on electronic Instron 5566 (Instron, United States). The injection specimens were all kept in an environment at 23°C and -20°C for 24h before performance test. Each specimen is measured five times, and the average value of the five groups of measured data was taken as the result.

3. Results and discussion

3.1 Molecular weight and molecular weight distribution
The possible thermal oxidative degradation or crosslinking in multiple extrusion process is noteworthy. Therefore, the changes of the molecular weight and distribution of the multi extrusion samples were investigated firstly. Fig.1 shows the GPC curves of IPC samples after multiple extrusion. For EP533N1-1 and EP533N2-1 samples, the molecular weight and molecular weight distribution have almost no change after multiple extrusion. Therefore, thermal oxidative degradation and crosslinking can be neglected because antioxidant was added in every extrusion.
Fig. 1 GPC curves of EP533N1-1, EP533N2-1, and the products after they underwent multiple extrusion.

3.2 Phase morphology evolution of IPC after multiple extrusions

Fig. 2 and Fig. 4 are the SEM image of the quenched section of EP533N1-1 and EP533N2-1 samples after multiple extrusion. The quenched sections were etched by n-heptane. Due to the strong etching ability of n-heptane to the EPR, the scattered holes observed on the surface after etching can be considered as the dispersed rubber phase in IPC. Fig. 3 and Fig. 5 give the statistical results of rubber granule size which were obtained by statistical analysis of SEM images by Image J software.

For sample EP533N1-1 with relatively lower molecular weight of EPR, it was observed that with the increase of extrusion times, the rubber granule size turned to smaller and the distribution of rubber phase became more uniform. In Fig. 2c, the rubber granules bigger than 3 μm almost disappeared, and the size of etched holes in sample EP533N1-3 concentrated between 0.4-2.0 μm after the third extrusion (Fig. 3c). For sample EP533N2 with relatively higher molecular weight of EPR, rubber granule size reduction and the more uniform distribution were also observed after the second extrusion (Fig. 4b), in which the holes diameter decreased to 0.2-1.2 μm (Fig. 5b) and the rubber granule larger than 1.8 μm almost disappeared. However, the size of rubber phase became larger and the distribution of rubber phase became wider significantly after the third extrusion (Fig. 5c). The rubber granules larger than 2.0 μm appeared again, which was obviously different from that of EP533N1-1 sample.

It is believed that during extrusion of multi-phase copolymer, the thermal effect can result in phase coarsening and shearing will promote the phase dispersing [14]. In general, the effect of shear-facilitated dispersion is strongly dependent on the molecular weight of the dispersed phase. The diverse phase structures of EP533N1-1 and EP533N2-1 series after multiple extrusion should be attributed to the difference in molecular weight of their EPR components. The rubber phase in EP533N2-1 has a relatively high molecular weight, so it took longer time or stronger shear energy to inhibit the agglomeration of rubber granules when the molecular chains of the rubber phase moved and dispersed. Therefore, under the same processing conditions as EP533N1-1 sample, agglomeration occurred during the extrusion process.
Fig. 2 SEM images of (a) EP533N1-1, (b) EP533N1-2 obtained by the second extrusion, (c) EP533N1-3 obtained by the third extrusion (for SEM observation, fracture surface of injection molding specimens were obtained at liquid nitrogen and then were etched in 23°C at n-heptane for 96 h)

Fig. 3 Statistical size of rubber granules in SEM by Image J software: (a) EP533N1-1, (b) EP533N1-2, and (c) EP533N1-3
Fig. 4 SEM images of (a) EP533N2-1, (b) EP533N2-2 obtained by the second extrusion, (c) EP533N2-3 obtained by the third extrusion (for SEM observation, fracture surface of injection molding specimens were obtained at liquid nitrogen and then were etched in 23°C at n-heptane for 96 h)

Fig. 5 Statistical size of rubber granules in SEM by Image J software: (a) EP533N2-1, (b) EP533N2-2, and (c) EP533N2-3
3.3 Thermal behavior

Fig. 6 and Fig. 7 show DSC curves of specimens EP533N1-1 and EP533N2-1 after multiple extrusion. It was revealed that the melting and crystallization behaviors of the sample changed little with the increase of extrusion times. The slight change is that the melting range of the sample after multiple extrusion was slightly narrowed, and the crystallization start temperature and crystallization end temperature were slightly increased. This indicates that the crystallization capacity of the crystallizable segments in the sample after multiple extrusion tended to be the same.

3.4 Mechanical properties

The mechanical properties of IPC samples after multiple extrusion were tested. It can be seen from Fig.8a and Fig.9a that no significant change was observed in the melt flow rates of EP533N1-1 and EP533N2-1 after multiple extrusion, indicating that the degradation of the samples could be ignored, which is consistent with the GPC results. The flexural modulus of the samples changed slightly. For EP533N1-1 series, it can be seen from Fig.8b that with the increase of extrusion times, the impact strength at room temperature increased, but the impact strength at low temperature decreased. For EP533N2-1 series, the sample after the second extrusion (EP533N2-2) exhibited the highest impact strength at room temperature, and the specimen after the third extrusion (EP533N2-3) displayed the highest value of low temperature impact strength. According to the results of impact properties and phase morphology of multiple extrusion, it is reasonable to inference that the small and uniform rubber granule size would improve the impact strength of IPC at room temperature, while larger rubber granule size was conducive to improving the impact strength at lower temperature, which is consistent
with Chen’s research \cite{14}.

Fig. 8 Mechanical properties of EP533N1-1, EP533N1-2 and EP533N1-3: (a) melt flow rate and flexural modulus, (b) impact strength at 23°C and -21°C

Fig. 9 Mechanical properties of EP533N2-1, EP533N2-2 and EP533N2-3: (a) melt flow rate and flexural modulus, (b) impact strength at 23°C and -21°C

4. Conclusions
In this work two typical IPC polymers, EP533N1-1 and EP533N2-1 were compared in phase morphology evolution and mechanical properties after multiple extrusion. It was discovered that the rubber phase size and distribution in IPC were significantly affected by the rubber phase molecular weight. When the molecular weight of rubber phase was relatively low, multiple extrusion would promote the refinement and dispersion of rubber phase. As the molecular weight of rubber phase increased, the size of rubber phase became unstable after multiple extrusion, and the rubber granules became coarsened and aggregated. Small and uniform rubber phase could improve the impact strength of IPC at 23°C, while relatively larger rubber phase size was conducive to improving the impact strength at -21°C.

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