

Effect of Feed Composition in Gas-phase Polymerization on Structure and Properties of In Situ Impact Polypropylene Copolymer

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ABSTRACT

In this work, three in situ impact polypropylene copolymer (IPC) samples were prepared through Ziegler-Natta catalyst only changing the feed composition (ethylene to ethylene and propylene molar ratio, C₂/C₂+C₃) in gas-phase polymerization reactor. Polymer (IPC) were characterized by solvent classification, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), successive self-nucleation and annealing (SSA), nuclear magnetic resonance (¹³C-NMR) and scanning electron microscopy (SEM). The mechanical properties of IPC samples were tested. The results indicate that with similar ethylene content, the feed composition which determines the content and structure of EPR and EbP component in IPC, further impacts the rubber phase size and distribution in IPC, plays a key role in determining the impact toughness of IPC.

KEY WORD : *In situ impact polypropylene copolymer, Feed composition, Long-sequence crystalline, Phase morphology, Impact toughness*

1. INTRODUCTION

In situ impact polypropylene copolymer (IPC) have been widely used in automobile parts, appliances, and other industrial uses in the last three decades because of the excellent

mechanical properties, especially at low temperature, due to its low impact resistance, and relatively low production cost^[1-5]. A typical in situ impact polypropylene copolymer is prepared by a two-step sequential polymerization

process, in which the first step is propylene homopolymerization to form homopolypropylene as continuous matrix and the second is ethylene and α -olefin situ gas-phase copolymerization to form dispersed phase for improving the impact resistance performance by the third and fourth generation spherical Ziegler-Natta catalyst. This together so-called "reactor granule technology" makes it possible to exploit a series of widely diversified, previously unavailable multiphase materials^[6-9].

IPC has been proved to consist of three parts, homopolypropylene, ethylene propylene random copolymer, a series ethylene-propylene segmented copolymers with different sequence lengths of polyethylene (PE) and polypropylene (PP) by TREF, SEM, NMR, DSC and other analytical methods in many researcher works^[10-16]. Consequently, this complex composition results in a special multiphase structure further determining the mechanical properties of IPC. However, the synthesis polymerization process parameters decides the multidispersity of the copolymer composition^[17].

There are many polymerization process parameters affecting the composition and multiphase structure of IPC. We can change isotacticity, molecular weight and relative molecular weight distribution of the homogeneous polypropylene matrix by adjusting the reaction temperature, the ratio of the cocatalyst to the external electron donor, the reaction residence time and the hydrogen concentration in first propylene homopolymerization step. Further, changing the composition, distribution and molecular

weight of ethylene and α -olefin biopolymer and phase structure by adjusting feed composition (C_2/C_2+C_α), hydrogen concentration and reaction temperature in ethylene and α -olefin gas phase copolymerization step. G. h. Zohuri reported hydrogen concentrating can significantly reduce the isotactic polypropylene in the Ziegler - Natta catalyst system^[18]. A. van.Reenen had also reports the effect of hydrogen concentration on the isotactic of polypropylene depending on whether adding external electron donor in polymerization system^[19]. Biao Zhang had reported the using dicyclopentylidimethoxysilane (Donor-D) as external electron donor relative to the cyclohexylmethyldimethoxysilane (Donor-C). The molecular weight of copolymer is higher, but the using of Donor-C as external electron donor relative to the Donor-D, the content of block copolymer and verage propylene sequence length is higher^[20]. But among the various polymerization process parameters, there is no detailed report on how the feed composition affects the structure, phase morphology and impact resistance of IPC samples.

The purpose of this work is three aspects. Firstly, using propylene as α -olefin, we synthesized three IPC samples by stably controlling other polymerization process parameters in gas phase reactors under different feed composition(C_2/C_2+C_3). Secondly, the structure of the three IPC samples were analyzed in detail. Finally, the relationship between the feed composition and the structure and properties of IPC samples were established, which has good industrial guiding significance.

2. EXPERIMENTAL

2.1. Experimental Materials

All water, oxygen sensitive operation processes were in high purity nitrogen protection. Cyclohexyldimethoxymethylsilane (Donor-C), AlEt_3 , were from Aldrich and used without further treatment. High purity polymerization grade propylene and ethylene and hydrogen were supplied by Lanzhou Petrochemical Co.

of Petro China. Ziegler-Natta catalyst, with the composition of Ti 2.43 wt%, Mg 18.3 wt%, diisobutyl phthalate 7.25 wt% and with the particle size (D50) of 50 μm .

2.2 Polymerization Plant

The IPC samples were prepared on gas phase reactor setup (Fig. 1), which consists of four reactors. The first reactor is propylene prepolymerization reactor, the second reactor and the third reactor are loop reactor,

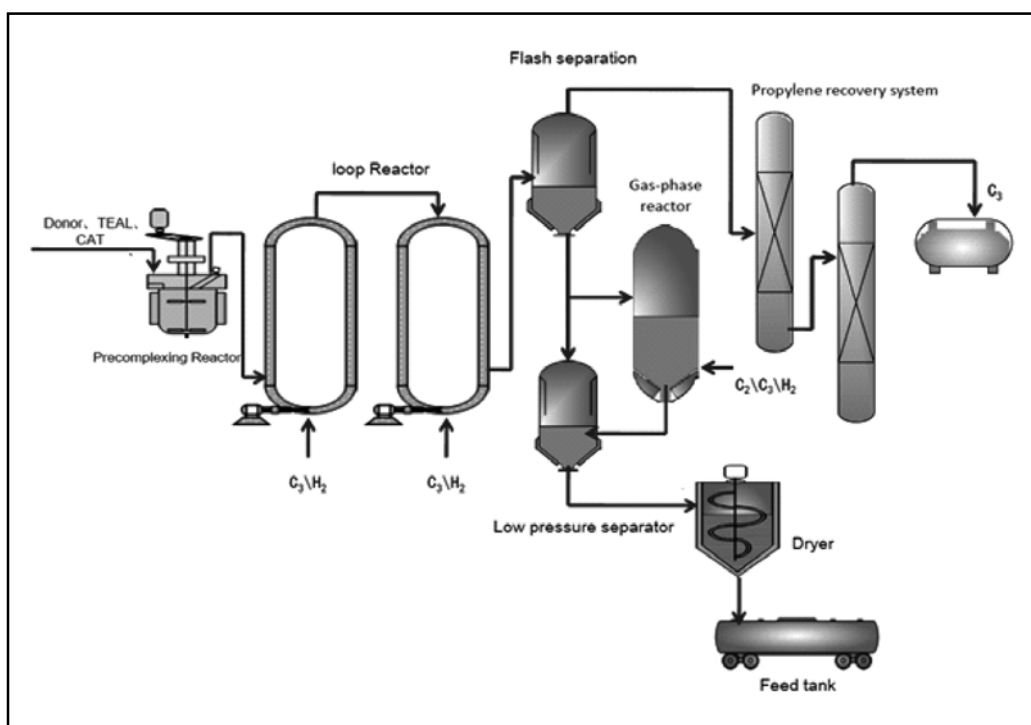


Fig. 1. Gas phase reactor

in which propylene is homogenized, and the fourth reactor is gas-phase fluidized bed reactor.

2.3 Synthesis of IPC

A typical Ziegler - Natta catalyst, with 2.43 wt% of Ti, 18.3 wt% of Mg, 7.25 wt% of diisobutyl phthalate as internal donor, and with the particle size (D50) of 50 μm . Cyclo-hexyldimethoxymethylsilane (ED-C) as external

donors, AlEt_3 as cocatalyst. IPC samples (IPC-1, IPC-2, IPC-3) were prepared only changing the feed composition ($\text{C}_2/\text{C}_2+\text{C}_3$, mol/mol) in gas-phase polymerization reactor. The polymerization conditions and results are summarized in Table 1. From Table 1, the prepared feed composition of IPC-1 is lower than IPC-2 lower than IPC-3 sample.

TABLE 1. Polymerization process parameters of IPC

	IPC-1	IPC-2	IPC-3
T1, °C	70	70	70
T/D, kg/kg	3	3	3
t1, min	90	90	90
H1, ppm	7000	7000	7000
T2, °C	80	80	80
t2, min	30	30	30
H2, ppm	5000	5000	5000
feed composition, mol/mol	0.183	0.291	0.367

T1: Loop reaction temperature, T2: Reaction Temperature of Gas Phase Polymerization

T/D, the ratio of AlEt₃ to ED-C.

t1: Loop Residence Time, t2: residence time of gas phase reaction.

H1: Hydrogen concentration in loop, H2: Hydrogen Concentration in Gas Phase Reactor.

feed composition: the ratio of ethylene to ethylene and propylene(C2/C2+C3).

2.4. Testing and Characterization

2.4.1 Ethylene content

The ethylene content of IPC samples were determined by Perkin-Elmer 2000 infrared spectrometer produced by PE Company in United States.

2.4.2 Solvent classification

IPC sample was placed in n-heptane, heat to 50 °C, stir it vigorously for 30 minutes, and then dry the filtered insoluble matter in vacuum. The filtrate was precipitated with acetone, and the precipitate obtained by vacuum drying was ethylene-propylene random copolymer (EPR). The above-mentioned n-heptane insoluble part was packed with copper mesh in a cable-type extractor and heated to the boiling temperature of n-heptane for 24 hours. The filtrate was precipitated with acetone. The resulting precipitate was filtered and vacuum-dried to obtain crystalline ethylene-propylene copolymer (EbP). The extracted insolubles were vacuum-dried to form isotactic polypropylene (HPP)^[14].

2.4.3 Molecular weight and molecular weight distribution

Molecular weight and molecular weight distribution 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.

2.4.4 Differential scanning calorimetry (DSC) and successive self-nucleation and annealing (SSA)

Differential scanning calorimetry (DSC) and successive self-nucleation and annealing (SSA) analysis: A DSC (DSC 214 Polyma, manufactured by NetzSCH Germany) with nitrogen as purge gas was used to probe crystallization and melting behavior of IPC samples and EPR, EbP, HPP component through solvent classification. Two different crystallizations, non-isothermal crystallization (cooling rates of 10 °C/min) and SSA experiments, were adopted. sample was heated to 200 °C for 10 min to eliminate thermal history. The exothermic and endothermic curves were all recorded. SSA experiment was carried out in accordance with the following steps: Firstly, sample was heated to 200 °C for 10 min to eliminate thermal history, after eliminating thermal history, then cooling down to 30 °C at a rate of 10 °C/min, then the sample was reheated to the first self-seeding temperature and keep at this self-seeding temperature for 10 min, at the temperature which almost all the crystals have been melted only very few crystal

fragments that could act as self-nuclei survived (Here, $T_s=153^\circ\text{C}$). Then this step was repeated every declining 5°C for self-seeding temperature and the scope of self-seeding temperature was chosen from 153 to 92°C . After completion of all the SSA process, the last melting curve was recorded^[21-23]. The detailed SSA steps are shown in Fig. 2.

2.4.5 Nuclear magnetic resonance (NMR)

^{13}C NMR spectra of the fraction were measured on a Bruker DMX400 Spectrometer at 100 MHz . Solutions ($10\text{wt}\%$) were prepared in *o*-dichlorobenzene. The spectra were recorded at 125°C . Broadband decoupling and a pulse delay of 5 s were used. Typically 6000 transients were collected.

2.4.6 Scanning electron microscope (SEM)

Scanning electron microscope (SEM) observation: Injection molding IPC samples were quickly quenched

after cooling in liquid nitrogen. In order to clarify the complex phase structure, the samples were adequately etched in xylene to remove the EPR content at 35°C for 4 h in ultrasound instrument, then drying in an oven for 1 hour at 60°C . After, quenching sections of these samples were all sputter-coated with gold powder were observed by SEM (XL-20 Scanning Electron Microscope Produced by Philips Company, Netherlands)^[24-25].

2.4.7 Mechanical properties

MFR was tested by PXRZ-400C melt flow rate meter produced by Ceast Company in Italy according to ISO 1133:1997. The notched 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. The flexural modulus was measured following ISO 178:1993 on electronic Instron 5566 (Instron, United States).

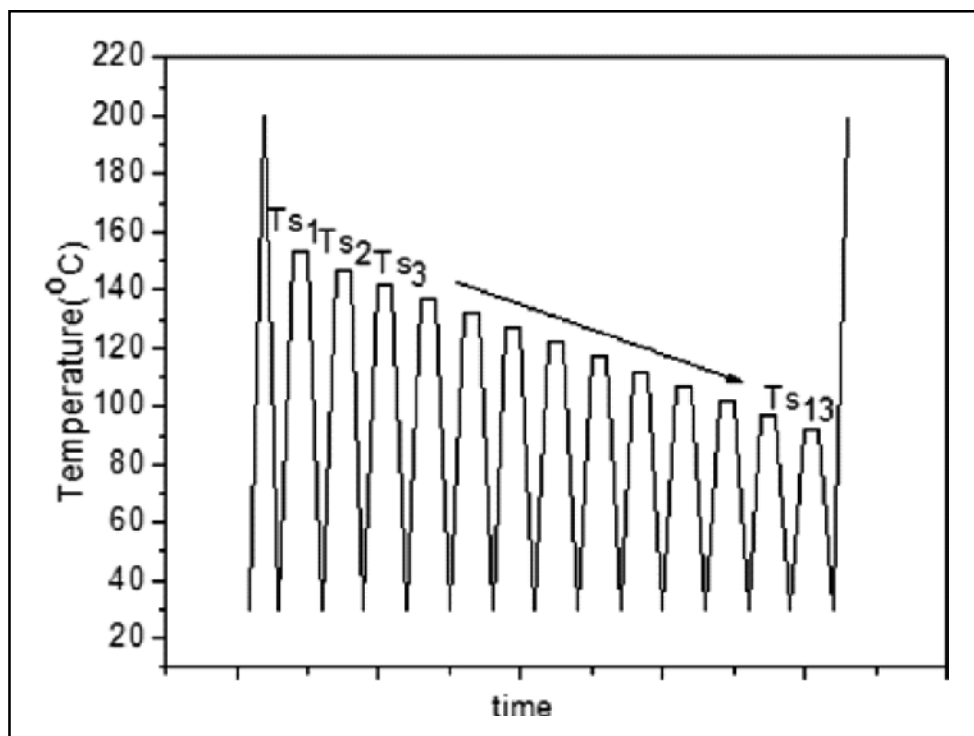


Fig. 2. Self-nucleation and annealing (SSA) steps

3. RESULTS AND DISCUSSION

3.1 Composition and molecular weight of IPC

The three IPC samples have similar ethylene content, molecular weight and molecular distribution, as shown in Table 2. Then the IPC samples were divided into three parts by solvent classification, random ethylene-

propylene copolymer (EPR), crystalline ethylene-propylene copolymer (EbP) and isotactic polypropylene (HPP), and the contents of each component of the three IPC samples are also summarized in Table 2. It can be seen from table 2, that the IPC-1 sample prepared in lower feed composition has more EPR and EbP component than that of the IPC prepared in higher feed composition.

TABLE 2. Ethylene content, composition and molecular weight of IPC

	IPC-1	IPC-2	IPC-3
C2, wt%	6.96	7.22	7.88
M _w ×10 ⁵ ,g/mol	2.316	2.219	2.198
M _n ×10 ⁴ , g/mol	2.06	2.11	1.99
Molecular weight distribution	11.24	12.03	11.45
EPR, wt%	7.49	5.34	4.95
EbP, wt%	10.62	9.39	9.07
HPP, wt%	81.89	85.27	85.98

3.2. Crystallization and melting behavior

Fig 3. gives the DSC curves of non-isothermal crystallization and corresponding melting behavior of IPC samples. Table 3 gives the relevant crystallization and melting data. The peak temperature during crystallization can reflect some degree of nuclear capability. The higher peak temperature is, the more easily chain segments can form. From Fig.3(a), The initial crystallization temperature ($T_{c-onset}$) of IPC-2 sample is higher than that of IPC-3 sample and higher than that of IPC-1 sample. So IPC-2 sample has more easily moving chain segments. The melting peak area is proportional to the quantity of chains participated in crystallization. IPC-3 sample

has bigger ΔH_c and ΔH_m , than that of IPC-2 sample and bigger than that of IPC-1 sample. So the crystallinity of IPC-3 is higher than that of IPC-2 and higher than that of IPC-1. From Fig. 3(b), the end melting temperature (T_{m-end}) of IPC-1 sample is higher than that of IPC-2 sample higher than that of IPC-3 sample, that is to say IPC-1 sample has the thicker lamellar length than that of IPC-2 sample higher than that of IPC-3 sample.

The EPR, EbP, HPP parts of the three IPC samples were analyzed by successive self-nucleation and annealing (SSA) (Fig. 4.). SSA technology is a continuous nucleation effect and can distinguish the subtle difference nucleation ability. Each melting peak is

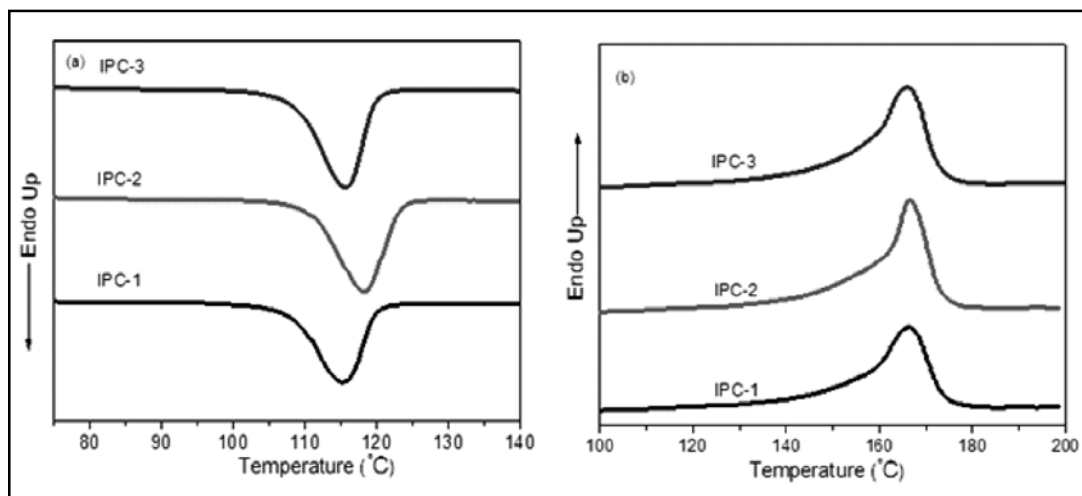


Fig. 3. DSC exothermic (a) and endothermic (b) curves through non-isothermal crystallization with cooling rates (R) of 10°C/min.

TABLE 3. DSC data for IPC samples

Sample	$\Delta H_c/$ (J·g ⁻¹)	H _m / (J·g ⁻¹)	T _c / °C	T _c -onset/ °C	$\Delta H_c/$ (J·g ⁻¹)	T _m / °C	T _m -end/ °C
IPC-1	75.77	60.46	115.3	119.9	75.77	166.4	173.6
IPC-2	85.82	70.97	118.3	123.1	85.82	166.5	173.1
IPC-3	87.81	71.51	115.7	120.1	87.81	166.1	172.8

ascribed to certain length crystallizable chain segments^[12]. In Fig.4 (a,b,c), EbP exhibits multiple melting peaks, HPP only one melting peaks while EPR is totally uncrystallized. Melting peaks in EbP are attributed to different lengths of PP and PE crystals.

In EbP component, the melting peaks, above 140°C, come from PP crystals with different lamellar thicknesses may result from the embedding of the ethylene units in the crystallizable propylene chain segments. These ethylene units act as defects and reduce the lamellae thickness of PP crystals. The melting peaks ranging from 100 to 130°C are from PE

crystals. It can be seen from the Fig.4(d), that EbP component of IPC sample prepared in different feed composition has different crystalline structure of polyethylene and polypropylene, especially polypropylene with different lamellar thickness (the melting peaks ranging from 140 to 160°C). In IPC-1 (EbP), the peak of the long-sequence polypropylene containing a small amount of ethylene moves toward high temperature, higher than that of IPC-2 (EbP), and higher than that IPC-3(EbP). This means that the lamellar thickness of long-sequence crystalline polypropylene containing a small amount of ethylene formed at low feed

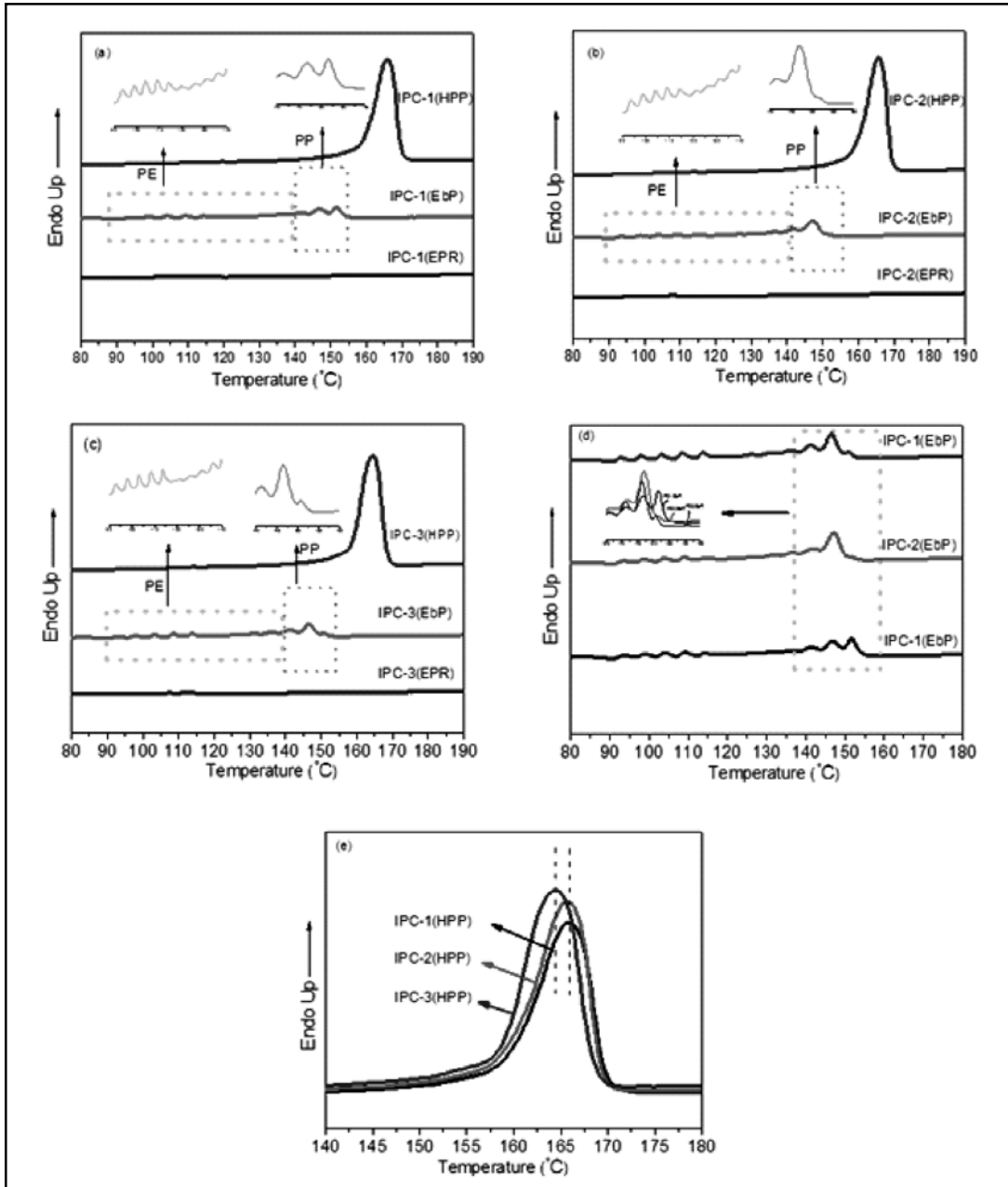


Fig. 4. DSC melting traces of IPC samples after SSA thermal treatment. To observe clearly, the curves of melting peaks of EbP presented at different scales. (a), (b), (c) are the EPR, EbP, HPP parts of the IPC-1, IPC-2, IPC-3. (d), (e) are respectively the EbP and HPP part of the IPC-1, IPC-2, IPC-3.

composition is thicker than that of IPC prepared at high feed composition.

It can be seen from the Fig. 4 (e), that HPP component of IPC sample prepared under different feed composition only has one melting peak, at about 165 °C. In IPC-1(HPP), the peak of the long-sequence polypropylene moves toward high temperature, higher than that of IPC-2(HPP), and higher than that of IPC-3(HPP), this means that the lamellar thickness of long-sequence crystalline polypropylene prepared at low feed composition is thicker than that of IPC prepared at high feed composition. This is consistent with the DSC analysis.

3.3. Chain structure

¹³C-NMR spectra of EPR, EbP and HPP of IPC-1, IPC-2, IPC-3 samples were measured to clarify the composition and chain structure. The results are summarized in Table 4. The

random ethylene-propylene copolymer (EPE+PEP) content in EPR part is higher than EbP component. The random ethylene-propylene copolymer (EPE+PEP) content and block part (EEP and PPE) content is zero in HPP part. It shows solvent classification of IPC by n-heptane having very good classification effect. The content of triad PPP of IPC-1(HPP) (95.69 wt%) part is more than IPC-2(HPP)(93.46 wt%), more than IPC-3 (HPP) (89.69 wt%), it shows IPC-1(HPP) having more long sequences of propylene chain segments which may be crystallization than IPC-2(HPP), more than IPC-3(HPP). The PPE+EPP sequence content of IPC-1(EbP) is 15.41 wt% which closes to IPC-2 (EbP) (15.75 wt%) but far more than IPC-3(EbP)(7.36 wt%), that is to say IPC-1(EbP) and IPC-2 (EbP) having more crystallizable block structure of polypropylene than IPC-3 (EbP), the results are consistent with the results of SSA.

TABLE 3. Sequence distribution (wt%) in the fractions for IPC samples

	IPC-1 (HPP)	IPC-1 (EbP)	IPC-1 (EPR)	IPC-2 (HPP)	IPC-2 (EbP)	IPC-2 (EPR)	IPC-3 (HPP)	IPC-3 (EbP)	IPC-3 (EPR)
E	4.31	38.00	40.04	6.54	49.63	47.82	10.31	48.06	30.21
P	95.69	62.00	59.96	93.46	50.37	52.18	89.69	51.94	69.79
EE	4.31	28.2	24.53	6.54	29.49	28.45	10.31	34.15	15.79
EP+PE	0	25.22	33.54	0	33.88	34.18	0	24.95	45.22
PP	95.69	46.58	41.93	93.46	36.63	36.36	89.69	40.9	38.99
EEE	4.31	22.59	16.14	6.54	14.1	19.45	10.31	25.97	7.99
EEP+PEE	0	11.21	16.77	0	30.77	20	0	16.36	15.59
PEP	0	4.20	7.13	0	4.76	8.36	0	5.73	6.63
EPE	0	7.71	9.64	0	5.86	9.82	0	7.36	8.97
PPE+EPP	0	15.41	16.77	0	15.75	12.00	0	7.36	43.66
PPP	95.69	38.88	33.54	93.46	28.75	30.36	89.69	37.22	17.15

3.4. Rubber phase distribution and mechanical properties

In recent ten years, many researchers have devoted to study the complex phase structure of IPC and have found the special scattered core-shell structure in PP matrix. The composition of core-shell structure had been confirmed by many works [27-29]. Similar results that a small amount of PE phase was surrounded by another small amount of EPR. PE and ipp matrix parts were connected by EbP as compatibilizer (such as grafted or segmented copolymer with long propylene sequences) and EPR^[18]. EbP core (rich with

long ethylene chain segments) and EbP bridge (rich with long propylene chain segments) were clearly observed when sample etched by xylene at 50°C but disappeared after being etched by xylene at 100 °C by the work of Biwei Qiu^[21].

Though the core-shell structure of IPC has been revealed by a lot of ways and characterization methods, however, the effect of feed composition in the gas phase polymerization reactor on the core-shell structure, the size and distribution of dispersed phase in IPC has not been reported in detail. The size of dispersed phase and the number of dispersed particle of IPC-1, IPC-2, IPC-3 are shown in Fig. 5. EbP core (rich in

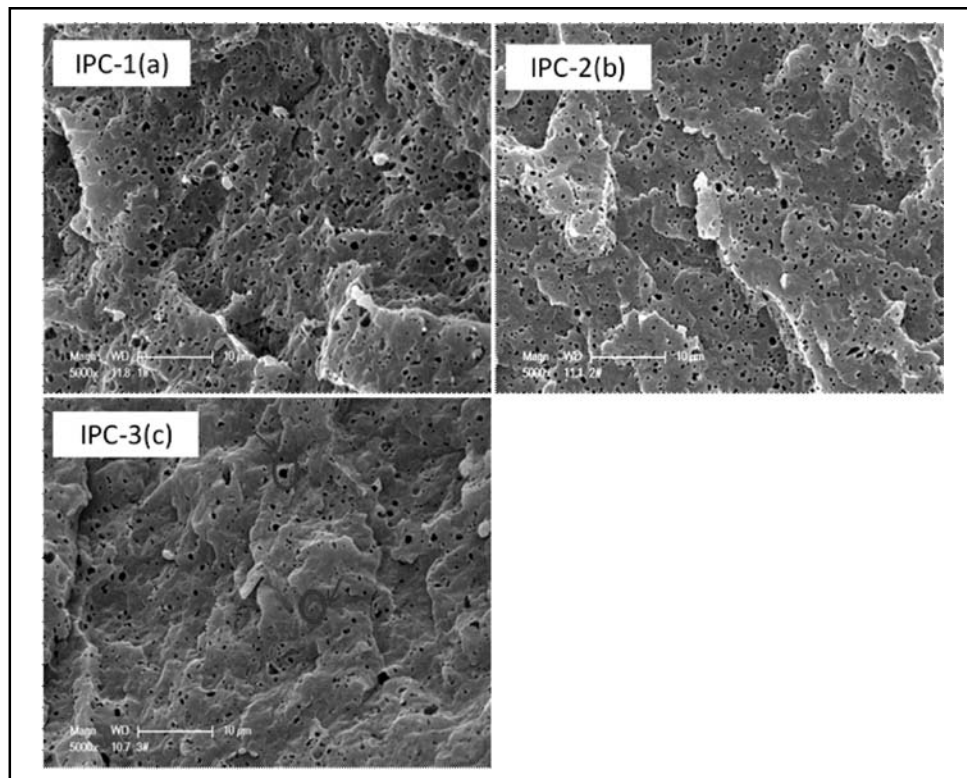


Fig. 5. Phase morphology of IPC with different magnifications after removing EPR (IPC etched in xylene for 4 h (etched at 35°C)).

long ethylene chain segments) and EbP bridge (rich in long propylene chain segments) weren't observed in these three IPC samples. In IPC-1 sample, the size and quantity of rubber phase are larger than that of IPC-2 sample, and the dispersion uniformity of IPC-1 sample is better than that of IPC-2 sample. The rubber phase content of IPC-3 sample is less than that of IPC-2, IPC-1 sample, and the distribution of dispersed phase is very uneven. That is to say when the IPC sample prepared under lower feed composition, it may have larger rubber phase size, more uniform rubber phase distribution and more rubber phase content.

The mechanical properties of the three IPC samples were tested, as shown in Table 4 with same ethylene content, the impact toughness of IPC-1 sample is larger than that of IPC-2 sample and larger than that of IPC-3 sample, the flexural modulus of IPC-1 sample is close to IPC-2 sample lower than that of IPC-3 sample. That is to say, besides ethylene content in the product, the impact resistance is mainly determined by the feed composition which determines the content and structure EPR and EbP and phase structure of IPC sample.

TABLE 4. Mechanical properties of IPC samples

Sample	Impact Strength (kJ/m ²)	Flexural Modulus, MPa
IPC-1	10.11	1011
IPC-2	6.23	1038
IPC-3	4.54	1165

4. CONCLUSION

Three IPC samples were prepared only changing feed composition (the ethylene to ethylene and propylene molar ratio) carried out in gas phase reactor, and the three IPC samples have similar ethylene content, molecular weight and molecular distribution. It was found the IPC sample prepared under lower feed composition has more EPR and EbP component than IPC prepared higher feed composition. EbP component in IPC sample prepared under low feed composition has thicker lamellar long-sequence crystalline polypropylene containing a small amount of ethylene. HPP component in IPC sample prepared under low feed composition has thicker lamellar of long-sequence crystalline

polypropylene. The IPC sample prepared under lower feed composition has larger rubber phase size, more uniform rubber phase distribution and more rubber phase content. The impact resistance of IPC sample prepared under low feed composition is better than that of prepared under high feed composition. So the feed composition which determines the content and structure of EPR and EbP and rubber phase size and distribution, plays an important role in determining the impact resistance of IPC.

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