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Mass transfer resistance in the production of high impact polypropylene

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ABSTRACT

Mass transfer resistance in the production of high impact polypropylene (hiPP) produced by a two-stage slurry/gas polymerization was investigated by field-emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. It is found that the formation of ethylene–propylene copolymer (EPR) phases in polypropylene (iPP) particle produced in the first stage slurry polymerization exhibits a developing process from exterior to interior. During the early stage of ethylene–propylene copolymerization, with lower content of copolymerized ethylene (7.4 mol%), the EPR phases occur only in the external layer of the particle, while at the later stage of the copolymerization with higher content of copolymerized ethylene (26.7 mol%), the elastomer phases distribute uniformly in the whole particle. This phenomenon is due to an effect of mass transfer resistance. The origin of mass transfer resistance is loosely agglomerate inclusions of low tacticity polypropylene within the semi-filled micropores inside the iPP particle. It is the inclusions inside the micropores that resist the diffusion of ethylene/propylene comonomers into the particle.

1. Introduction

High impact polypropylene (hiPP) with both high rigidity and toughness is usually produced by a multistage polymerization process [1,2]. First, isotactic polypropylene (iPP) particles with high porosity are produced by gas or slurry polymerization, while in the second stage, which is always in gas phase, ethylene/propylene comonomers diffuse into iPP particles and form ethylene–propylene copolymer (EPR) phases in the iPP matrix.

As a product of the process, the heterophase of hiPP is established directly during polymerization. To further understand the morphological characteristics of hiPP particles is of great importance since it is closely related to the catalyst/polymer particle growth mechanism and the mass transfer aspect, as well as the catalyst design and polymerization control.

The structure of hiPP particle is determined by architecture of its precursor iPP particle and subsequent formation and location of the EPR phase inside the iPP matrix. It is believed that the iPP particle exhibits two structural characteristics [3–6], i.e., the multiple-grain architecture with the iPP particle composed of many subparticles and the subparticle in turn composed of many primary particles, and the pore network structure consisting of the macropores between the subparticles and the micropores inside the subparticles. The porosity is preliminary for the accessibility of the ethylene/propylene comonomers to the active catalyst centers in the iPP matrix during the second stage copolymerization, and therefore determines the accommodation and distribution of the EPR phase inside the iPP particle. As for the formation of EPR, there are still some debates. Debling and Ray [7] and McKenna et al. [8,9] proposed that EPR first forms on the catalyst sites underneath the iPP layer of the primary particles, and then expands or flows into the micro- and macropores. Cecchin et al. [10] suggested that EPR only forms on the surface of the subparticles and fills the pores between them. Very recently, Urdampilleta et al. [11] found that EPR forms in the iPP matrix, yielding a composite morphology, and some of the elastomer flows to the pores and the outer surface of the iPP particles.

In general, mass transfer limitations are related to the rate of polymerization. For the first stage homopolymerization, it is agreed that the mass transfer effects will be important only during the early stage of the polymerization [12,13]. For the second stage copolymerization, it is found that the rates of the polymerization usually decrease during the late stages of the polymerization if the particles maintain sufficient porosity [14,15], while McKenna and Kittilsen [8] found that, after a critical copolymer content (40%), the transformation of the internal morphology can provoke mass transfer resistance. However, to our knowledge, there is no report on mass transfer resistance based on morphological study up to date.

In our previous paper [16], we reported in detail the morphology, including the multiple-grain architecture and pore network structure of iPP particle, and the formation process of the EPR phase

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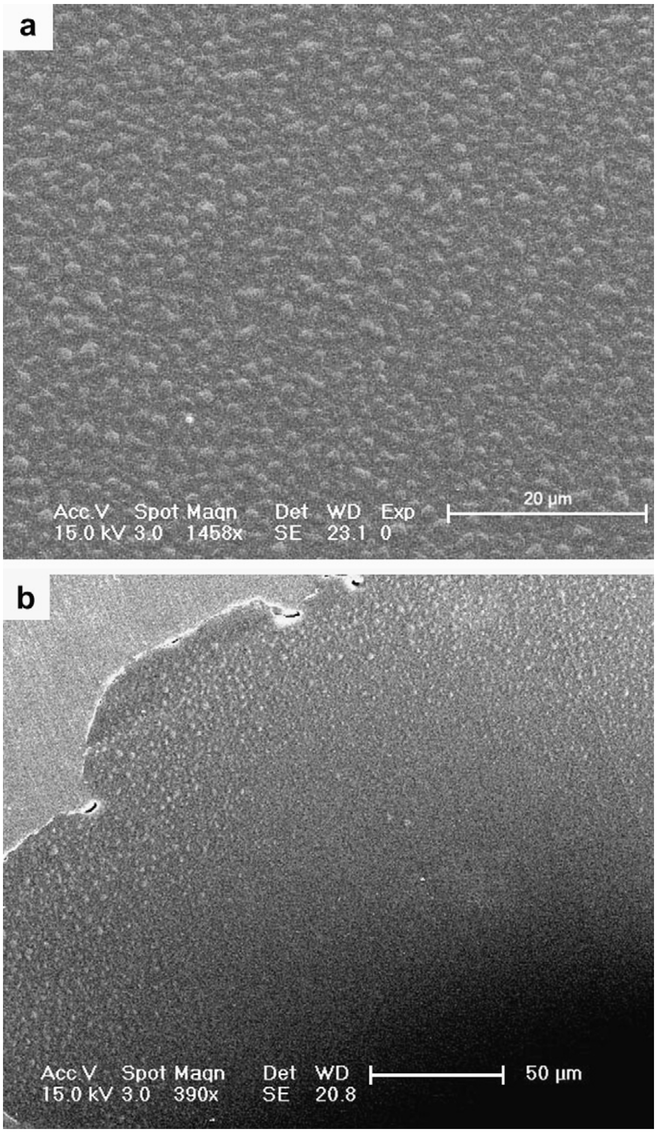

Fig. 1. SEM micrographs of the cross-section of (a) a hiPP-1 particle and (b) a hiPP-2 particle.

in hiPP produced by a two-stage gas/gas polymerization. In the present work, a two-stage slurry/gas polymerization was adopted for the hiPP production. A kind of semi-filled micropores with loosely agglomerate inclusions of low tacticity polypropylene in them were found, and the mass transfer resistance was discussed in terms of the morphological observations for the first time.

2. Experimental section

2.1. Materials and sample preparation

A two-stage polymerization was adopted using high activity $TiCl_4/MgCl_2$ catalyst. The iPP homopolymer particles were produced in bulk slurry at 80 °C under a high-pressure. The second stage ethylene–propylene copolymerization was performed in gas phase. By controlling the copolymerization time, two kinds of hiPP particles with different ethylene contents were obtained, i.e., hiPP-1 with ethylene content of 26.7 mol% and hiPP-2 with ethylene content of 7.4 mol%, as determined by ^{13}C NMR. Only one particle (ca. 0.6 mm in diameter) of iPP and hiPP was separately imbedded in EPON™ 812 resin and then cryosectioned with glass knife in a Leica Ultracut R microtome operated at −90 °C and a cutting speed of 1 mm/s.

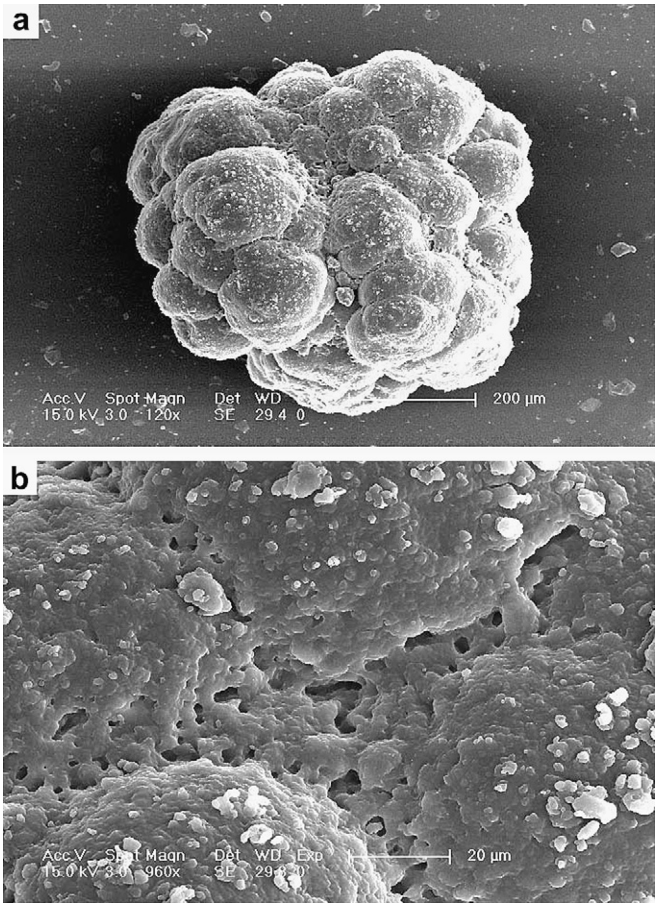

Fig. 2. SEM micrographs of the external morphology of an iPP particle: (a) overview of an iPP particle; (b) magnified image of (a).

2.2. Measurements

The iPP particle as well as the cut surfaces were coated with Au and then examined with an XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. Some samples (including cut surfaces and iPP particles) were extracted with xylene for 60 min at room temperature and 80 °C, respectively, before observation.

For TEM observation, thin section (ca. 50–100 nm thick) of the particle was transferred onto copper grids and then stained with RuO_4 vapor for 7 h at 30 °C. A JEOL 1011 TEM operated at 100 kV was used.

3. Results and discussion

In order to observe the effect of copolymerized ethylene content on EPR phase formation during the second stage gas polymerization, the cut surfaces of hiPP-1 and hiPP-2 particles with different ethylene contents were examined first. Fig. 1(a) shows the SEM micrograph of the cut surface of a hiPP-1 particle with higher ethylene content of 26.7 mol%. In the SEM image, the protruded grains with relatively bright contrast represent EPR phases (we will explain why the EPR phases protrude from the cut surface below). It is clear that the EPR phases disperse uniformly on the cut surface of hiPP-1 particle. However, for hiPP-2 particle with lower ethylene content of 7.4 mol%, the cut surface exhibits an unusual surface morphology (Fig. 1(b)). The distribution of EPR phases displays marked non-uniformity. Both the number and size of the elastomer phases decrease gradually from skin to core of the particle, and there is no EPR phase in the center. This phenomenon reflects directly the development process of EPR phases during the second stage copolymerization, i.e., from exterior to interior of the particle. It implies that there is something within the particles which limits the diffusion of ethylene/propylene comonomers into the particle, i.e., producing a mass transfer resistance effect. Undoubtedly, this resistant material must result from the interior of iPP particle (which is the precursor of hiPP particle). In order to clarify the origin of the mass transfer resistance, we must examine in detail the morphology of iPP particle produced in the first stage slurry polymerization.

The apparent morphology of the iPP particle is similar to that obtained by gas phase polymerization, i.e., exhibiting a multiple-grain structure. Fig. 2(a) shows the SEM micrograph of a single iPP particle. The particle is composed of several tens of subparticles with diameter ranging from tens to hundred microns. The magnified image of the subparticle (Fig. 2(b)) shows that there exist macropores between the subparticles, while almost no micropores on the external surface of the subparticles are observed, which is different from the surface morphology of the iPP particle produced by gas phase polymerization, on which many micropores are observed, as reported in our previous paper [16].

For a direct observation of the internal structure of the iPP particle, the particle is cut by cryomicrotomy. Fig. 3(a) shows the SEM micrograph of the cross-section of an iPP particle. Only a few large cavities in the cut surface of the particle can be observed. Fig. 3(b) presents a magnified image of the cavity indicated by the arrow in Fig. 3(a). Clearly, the cavity represents macropore between the subparticles. The quite small number of the macropores existing inside the particle implies that most of the subparticles agglomerate together tightly during their growing. Fig. 3(c) is a magnified SEM image of the cut surface of Fig. 3(a) taken at a location without macropores. Surprisingly, the cut surface of the particle is rather smooth, and almost no apparent micropores are observed at all, which is markedly different from the results obtained in our previous work [16]. For the convenience of the reader, the SEM image of the porous cut surface of an iPP particle produced by gas polymerization is shown in Fig. 3(d). Now the question is whether the micropores do indeed not exist inside the particle and if it is so, how the ethylene/propylene comonomers can diffuse into the iPP particle and form the EPR phases during the second stage gas copolymerization.

In order to further understand whether the micropores exist inside the iPP particle, thin section of the particle is observed with TEM, which will provide internal structural details of the particle. Fig. 4(a) shows a bright field electron micrograph of thin section of the particle after staining with RuO_4 for 7 h. The darker regions are iPP matrix stained with RuO_4, while the relatively light irregular regions, with size of hundreds of nanometers, are holes or gaps in the sections. Unambiguously, these holes or gaps correspond to the micropores inside the iPP particle. It should be pointed out that the micropores seem to be not completely empty, but contain some inclusions. This is different from the result of our previous work [16]. The iPP particle produced by gas polymerization contains a large amount of empty micropores. For comparison, a TEM image of thin section of the iPP particle produced by gas polymerization is presented in Fig. 4(b). Judged from the image contrast of Fig. 4(a), the inclusions are loosely agglomerative within the micropores. In other words, the micropores are loosely filled or semi-filled, and this is just the reason that the micropores could not be observed by SEM on the cut surface of the iPP particle (Fig. 3(c)) although they do indeed exist. In addition, it is also noticed that the iPP matrix (the darker regions in Fig. 4(a)) is composed of many small globules,

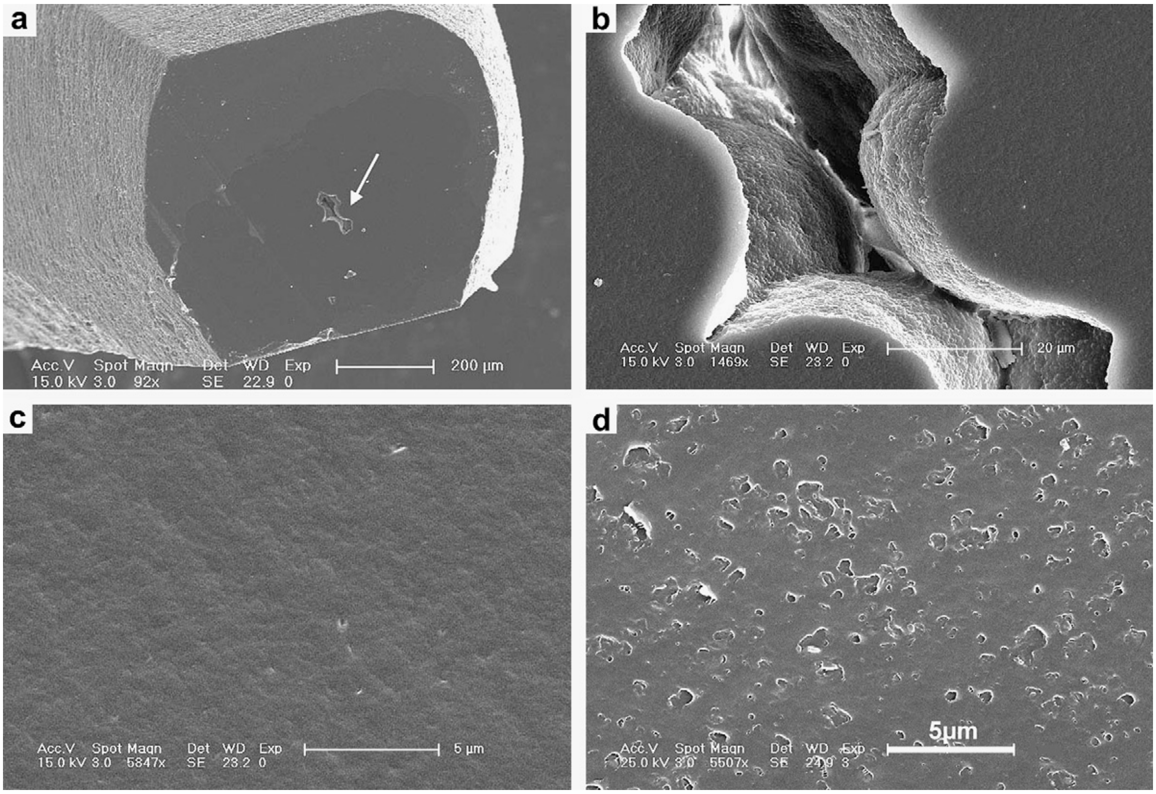

Fig. 3. (a) SEM micrograph of the cut surface of an iPP particle produced by slurry polymerization; (b) a magnified image of the macropore indicated by an arrow in (a); (c) a magnified image of (a) taken in the location without macropores; (d) magnified SEM micrograph of the cut surface of an iPP particle produced by gas polymerization (Ref. [16]).

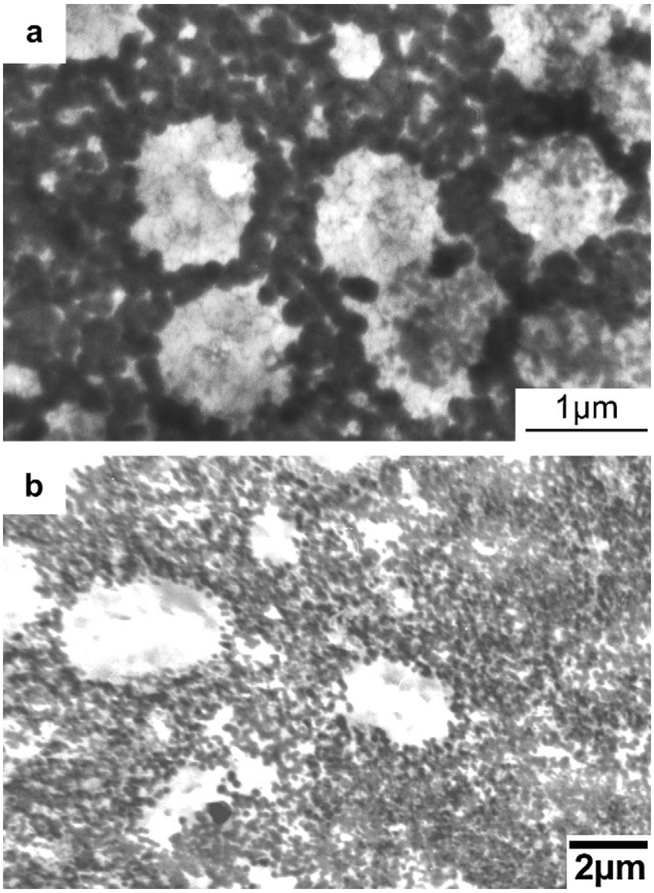

Fig. 4. TEM micrographs of the thin section of an iPP particle produced by (a) slurry polymerization and (b) gas polymerization (Ref. [16]), after staining with RuO_4 for 7 h.

ca. 100 nm in diameter, which are considered to be the primary particles, i.e., the smallest building blocks of the iPP particles [16].

Solvent extraction experiments were used to determine the material composition of the inclusions within the micropores inside the iPP particle. Fig. 5(a) and (b) shows the SEM micrographs of the cut surface of the iPP particle after solvent (xylene) extraction for 60 min at room temperature and 80 °C, respectively. The cut surface etched at room temperature exhibits less micropores with small size (Fig. 5(a)), while the one etched at 80 °C displays a large number of micropores with larger size (Fig. 5(b)). The results indicate that the materials semi-filled in the micropores of the iPP particle are etched out by xylene. The materials solved at room temperature should be atactic polypropylene, while those etched out at 80 °C should be the polypropylene with lower tacticity. In addition, the solvent experiments of iPP particles further confirm the above results. When the particles are extracted at room temperature, only a very small amount of atactic polypropylene is obtained from the extraction solution, and for the one extracted at 80 °C, the amount of low tacticity polypropylene (with melting point of 127 °C) obtained is about 1.0 wt%.

Clearly, it is the inclusions within the micropores in iPP particle that become the origin of mass transfer resistance during the second stage gas copolymerization. Due to the existence of inclusions inside the micropores, even if they are loosely agglomerate, the diffusion of ethylene/propylene comonomers into the iPP particle must be limited, resulting in great decrease of the diffusion rate of ethylene/propylene comonomers. It should be pointed out that there exists a competition between the mass transfer and the polymerization. In this case, the reaction rate must be much faster than the diffusion rate. As a result of the competition of the two rates, during the early stage of copolymerization (with shorter reaction time), e.g., in the case of hiPP-2, the EPR phases will form only in the external layer (Fig. 1(b)), and gradually develop towards the interior of the particle with the copolymerization proceeding as well as the decrease or depletion of catalyst activity in the external layer. Only at the late stage of copolymerization (with longer reaction time), e.g., in hiPP-1, the elastomer phases could attain a uniform distribution in the whole particle (Fig. 1(a)). The above mechanism is shown by a model of Fig. 6. It should be noted that the proposed mechanism works only when the reaction rate is much faster than the diffusion rate in gas polymerization. On the contrary, if the diffusion rate is faster than the reaction rate, i.e., in the circumstances where there is almost no marked mass transfer resistance, even at the early stage of copolymerization with less formation of EPR, the elastomer phases will distribute uniformly in the whole particle.

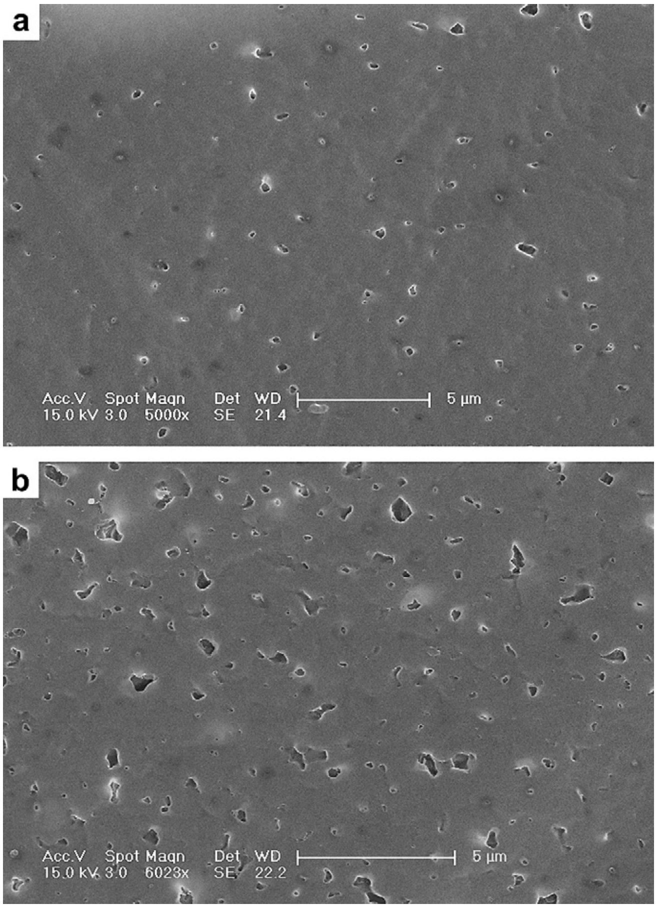

Fig. 5. SEM micrographs of the cross-section of the iPP particle, after solvent extraction for 60 min at (a) room temperature and (b) 80 °C.

Of course, there are many factors that affect the formation of EPR phase. In addition to the amount of copolymerized ethylene, the catalyst feature and morphology, polymerization condition, and

Fig. 6. A schematic showing the development of EPR phases in the iPP particle during the second stage copolymerization.

the catalyst productivity, etc., have important effect on EPR phase formation. Further research work will be done in the future.

Finally, we will discuss why the EPR phases protrude from the cut surface of hiPP particle, as shown in Fig. 1. A reasonable explanation is that the EPR phases, during their formation process in the semi-filled micropores inside the iPP particle, must squeeze out the inclusions that originally existed in the pores, and therefore they have larger inner-stress. After being cryosectioned, the inner-stress of the EPR phases is released, resulting in volume expansion of the elastomer phases and protruding from the cut surfaces. This phenomenon is different from our previous result [16]. The cut surface of the hiPP particle produced by a two-stage gas/gas polymerization is very smooth (see Fig. 5(b) in Ref. [16]) and no protruded EPR phase was observed. The hiPP particle produced by gas/gas polymerization contains empty micropores, rather than semi-filled micropores. Therefore, the EPR phases do not produce inner-stress during their formation process in the second stage copolymerization, and thus the EPR phases could not protrude from the cut surface of the hiPP particle after being cryosectioned.

4. Conclusions

The iPP particle produced by the first stage slurry polymerization contains a large number of semi-filled micropores with loosely agglomerate inclusions of low tacticity polypropylene. The inclusions within the micropores will limit the diffusion of ethylene/propylene comonomers into the particle. As a result of the mass transfer resistance, the formation of EPR phases in the iPP particle during the second copolymerization undergoes a developing process from exterior to interior. During the early stage of copolymerization, the EPR phases are produced merely in the external layer of the particle, while only at the late stage of copolymerization, the elastomer phases will develop to the interior of the particle, exhibiting a uniform distribution in the whole particle.

Acknowledgements

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