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Morphology of high impact polypropylene particles

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Abstract

Morphological features of isotactic polypropylene (iPP) and high impact polypropylene (hiPP) particles produced in a multistage polymerization process were investigated by field-emission electron microscopy (FESEM) and transmission electron microscopy (TEM) techniques. Study was mainly focused on architecture of iPP particle and distribution of elastomer phase (EPR) within the preformed iPP matrix. The iPP particle is an agglomerate of many subglobules (ca. several to hundred microns in diameter), while the subglobule in turn is formed by a great deal of primary globules (ca. 100 nm in diameter). Large macropores between the subglobules and finely distributed micropores within the subglobule constitute a network of pore inside the iPP particle. Ethylene/propylene comonomers can diffuse into the macro- and micropores and copolymerize on catalyst active sites located on periphery of the pores, forming elastomer phase inside.

Keywords: High impact polypropylene; Morphology; Multistage polymerization

1. Introduction

High impact polypropylene (hiPP) is an important commercial polyolefin usually produced with $TiCl_4/MgCl_2$ catalyst in a multistage polymerization process. In the first stage, isotactic polypropylene (iPP) particles are produced, and in the second stage a rubbery ethylene–propylene copolymer phase (EPR) is produced within the preformed iPP matrix. The hiPP particles after polymerization can be used directly without pelleting and the material exhibits superior rigidity–toughness balance [1,2].

As an in situ product of polymer blends, a detailed knowledge of morphology of the hiPP particle will be helpful not only in understanding the structure–property relationship of this material, but more importantly, in comprehending and rationalization of the particle growth mechanism associated with polymerization kinetics and catalyst design.

So far, investigations on the hiPP particle morphology are mainly focused on two aspects. (1) Architecture of the iPP particle. The particle growth in olefin polymerization is usually described by the ''multi-grain model'' [3]. In this model, the catalyst grain consists of much smaller fragments. Monomers polymerize on active centers of the catalyst fragments, forming a polymer shell and causing the catalyst grain to expand progressively as polymerization proceeds (a catalyst-to-polymer replication phenomenon [4–8]). However, the iPP particles formed during the production of hiPP exhibit a multiple structure, which can be better represented by the ''double-grain model'' proposed by Bukatov et al. [9,10]. Kakugo et al. [11–13] reported that the iPP particle is composed of many subparticles (ca. 1 μm). Each subparticle consists of tens of primary polymer globules (ca. 0.2–0.35 μm). Urdampilleta et al. [14] found that the iPP particle is formed by a small number of mesoparticles (subparticles), which have much bigger average size than that observed by Kakugo et al.

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In each mesoparticle, the catalyst fragments are well dispersed and all mesoparticles are equally reachable for the monomers. For whatever model proposed, the porosity of iPP matrix is critical for the production of hiPP: low porosity for iPP particles having sufficiently high bulk density to replace pellets, high porosity for incorporation and dispersion of the rubbery phase in the iPP particles. (2) Distribution of the EPR inside the preformed iPP matrix, which affects the impact properties of hiPP, as well as the mass transfer and particle sticking problems in the copolymerization stage. Most research supports a ''pore-filling model'', where EPR tends to locate around the homopolymer globules and fills the pores that are in-between. However, the mechanism of EPR formation seems still in debate. Debling and Ray [15] and McKenna et al. [16,17] proposed that EPR forms on the catalyst active sites underneath the iPP layer of primary globules, but progressively expands into the micropores separating the primary globules and then into larger macropores between the subparticles (agglomerate of the primary globules). However, Cecchin et al. [18] found that EPR only forms on the surface of the subparticles. Urdampilleta et al. [14] showed that most of EPR is finely dispersed within the mesoparticles (subparticles), while some EPR breaks the iPP matrix and flows to the macropores between the mesoparticles, and as polymerization goes on, tends to smooth the surface of iPP particle.

It is known that each model as mentioned above has merits in explaining the experimental phenomena observed therein. However, for the complexity of hiPP system, there is still a lot of work to do in understanding the hiPP morphology and the particle growth mechanism. In this study, structural details of the iPP and hiPP particles were further investigated by field-emission electron microscopy (FESEM) and transmission electron microscopy (TEM) techniques.

2. Experimental section

2.1. Materials and sample preparation

A two stage polymerization was conducted using high activity $TiCl_4/MgCl_2$ catalyst. The iPP and hiPP particles were obtained separately after the homopolymerization and copolymerization processes. The particles (ca. 1 mm in diameter) were imbedded in EPON™ 812 resin and then sectioned with glass knife in a Leica Ultracut R microtome operated at −90 °C and a cutting speed of 1 mm/s.

2.2. Measurements

The particles as well as the cross-section 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 were extracted with xylene for 30 min at room temperature before observation.

For TEM observation, thin sections (ca. 50–100 nm thick) of the particles were transferred onto copper grids and then stained with RuO_4 vapour for different time at 30 °C. A JEOL 1011 TEM operated at 100 kV was used.

3. Results and discussion

3.1. Morphology of the iPP particle

It is known that the iPP particle obtained during the production of hiPP always displays a multiparticle structure. This was also observed in the present study. An overview of a single iPP particle is shown in Fig. 1(a). Clearly, this particle is composed of many (maybe hundreds of) secondary globules with diameter ranging from several to hundred microns, which may reflect a similar multiparticle architecture of the catalyst grain in light of the replication effect during particle growth. These subglobules are much bigger and regular than that observed by Kakugo et al. [11–13], but seem more consistent with the proposed model of Urdampilleta et al. [14]. In addition, the magnified image of the subglobule (Fig. 1(b)) shows that the external surface of the subglobule is porous, with irregular pores ca. tens of nanometers to several microns in size.

For a direct observation of the particle internal structure, the particle is cut by cryomicrotomy. Fig. 2(a) shows an overview of the interior of a iPP particle. Some large cavities inside the particle can be observed. These cavities are considered to be macropores between the subglobules (compared with the much smaller micropores observed within the subglobules as shown below). Fig. 2(b) shows a magnified image of the macropore indicated by the arrow in Fig. 2(a), where subglobules, ca. several to tens of microns in diameter, and

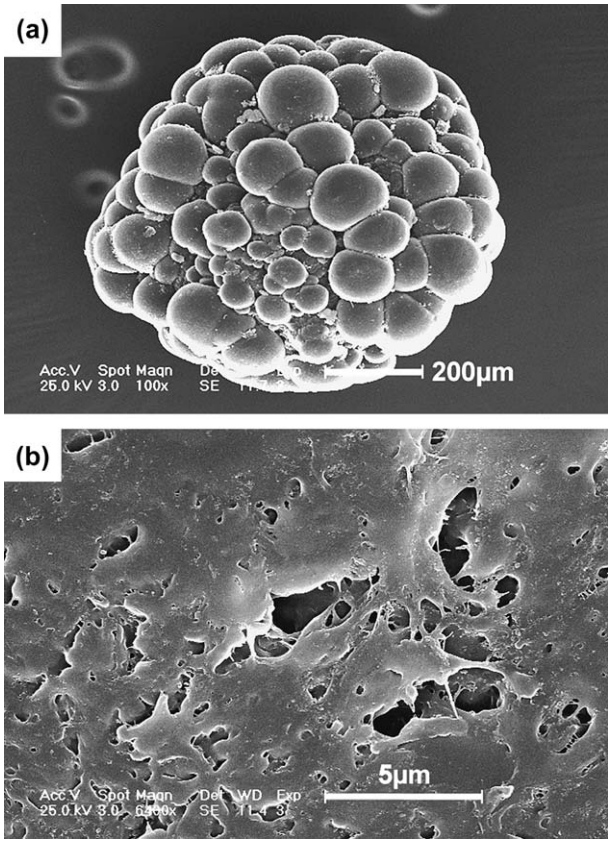

Fig. 1. SEM micrographs of the external morphology of iPP particle: (a) overview of a iPP particle; (b) external surface of a subglobule.

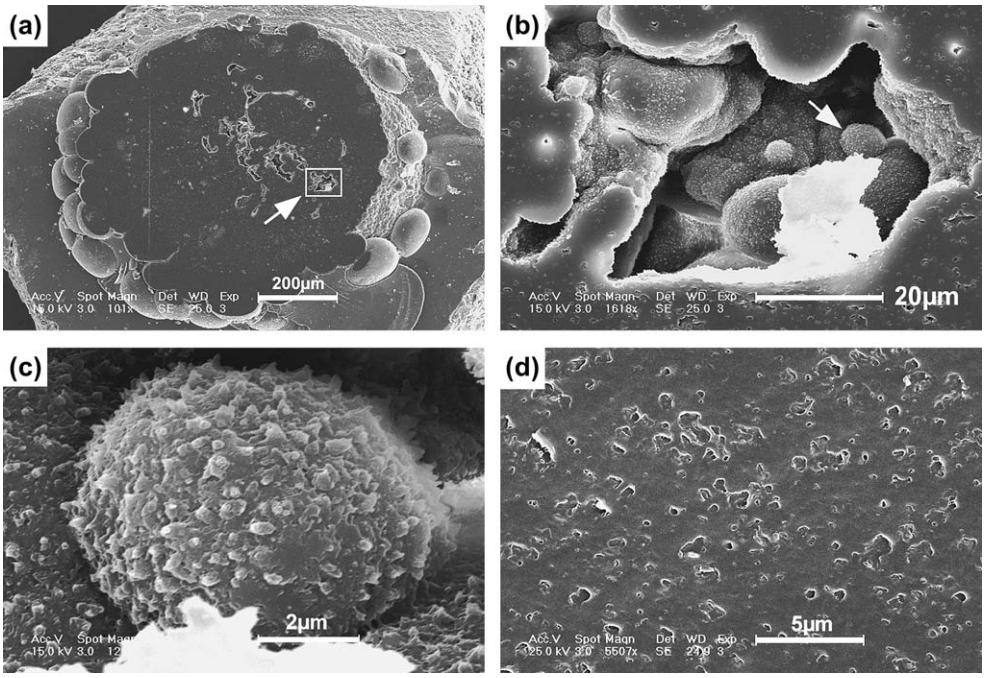

Fig. 2. SEM micrographs of the internal morphology of iPP particle: (a) overview of the cross-section of the particle; (b) a magnified image of the macropore indicated by an arrow in (a); (c) a magnified image of the subglobule indicated by an arrow in (b); (d) the interior structure of the subglobule.

their agglomerates are found inside the macropores. Fig. 2(c) is a magnified image of the subglobule indicated by the arrow in Fig. 2(b), which indicates that the subglobule is made up of much smaller particles, ca. 100–200 nm in diameter. These finer units should be primary particles of iPP (see also the TEM result below) with catalyst fragment inside. It should be noted that these primary particles cannot be readily found from the external surface of the subglobules located outside of iPP particle (Fig. 1(b)), and the subglobules inside the macropores are generally smaller than that observed from the outer surface of iPP particle (Fig. 1(a)). This observation indicates that the mass transfer limitations may occur, to some extent, during the polymerization as the iPP particle grows. However, this effect should be minor because the interior of these subglobules, both inside and outside of the iPP particle, exhibits porosity, as shown in Fig. 2(d).

TEM observation provides further structural details of the iPP particle (Fig. 3). Fig. 3(a) shows bright field (BF) electron micrograph of thin section of a subglobule of iPP particle after treated with RuO_4 vapour for 7 h. The darker regions are polypropylene matrix stained with RuO_4, while the irregular white domains, with size of hundreds of nanometers to several microns, are holes or gaps in the sections, corresponding to the micropores as observed by SEM (Fig. 2(d)). Higher magnification (Fig. 3(b)) indicates that the polypropylene matrix is composed of many small globules, ca. 100 nm in diameter, which are considered to be the primary particles, i.e., the smallest building blocks of the iPP particle, as observed by SEM (Fig. 2(c)). The primary globules are loosely packed and some of them form agglomerates. However, these agglomerates exhibit no regular structures as Kakugo et al. observed [11–13]. Although more compact stacking of the primary globules is also observed in the experiment, formation of the micropores within the subglobule, especially those with larger size as shown in Fig. 3(a), appears not only to result from the agglomeration of the primary globules but also to be a combined effect of the original catalyst architecture, its fragmentation with polymer growth, as well as the polymerization control. It is also noticed that the entire polypropylene primary globule can be stained with RuO_4, indicating a lower crystallinity of the primary globules, which is beneficial for the melt processing of the particles [1,2].

The above results indicate that there is an effective network of pores inside the iPP particle, including the macropores between the subglobules and the micropores within the subglobule. Unambiguously, this porosity of iPP particles is preliminary for the accessibility of the ethylene/propylene comonomers, which are fed in the second stage, to the active centers in the iPP matrix, and therefore determines the accommodation and distribution of the EPR phase inside the iPP particle. The uniform distribution of the pores within the subglobules also suggests that each subglobule may behave as a microreactor with its own mass and energy balance and the associated kinetics. In addition, the multiple construction of the iPP particle, from the primary globule to subglobule, reflects similar multiparticle texture of the original catalyst grain, which has different levels of organization and can undergo easy and extensive fragmentation upon polymer growth [4–10].

3.2. Morphology of the hiPP particle

The main interest associated with the hiPP particle morphology is the formation and distribution of EPR phase within

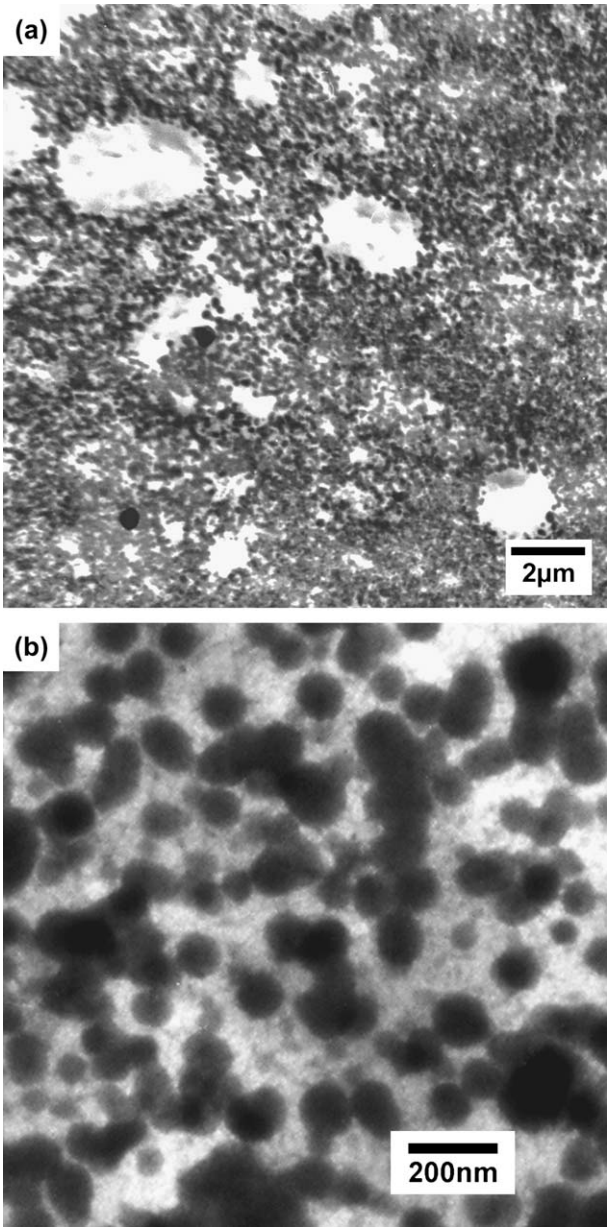

Fig. 3. (a) BF electron micrograph of thin section of a subglobule of iPP particle after stained with RuO_4 for 7 h; (b) a magnified image of the polypropylene matrix, displaying the primary globules.

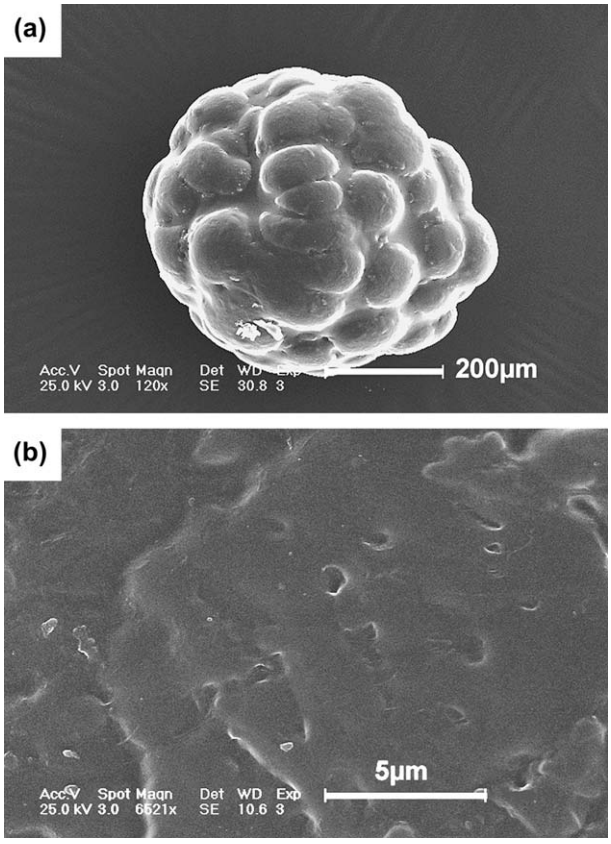

Fig. 4. (a) SEM micrographs of the external surfaces of a hiPP particle; (b) the subglobule.

the pre-existing iPP matrix. Fig. 4 shows FESEM micrographs of the external morphology of a hiPP particle. The overall surface of the particle (Fig. 4(a)) and that of the subglobule (Fig. 4(b)) are relatively smooth compared with that of the iPP particle (Fig. 1(a) and (b)), suggesting that the EPR fills the macro- and micropores appeared on the surface of the iPP particle. However, contours of the subglobules and some shallow pits on the subglobule surface can still be identified, indicating that the iPP particle is not totally covered by the EPR (which is essential for the free flowing of hiPP particles in the reactor and subsequent processing). An overview of the cross-section of the hiPP particle, as well as the internal surface of a subglobule inside the hiPP particle, is shown in Fig. 5(a) and (b), respectively. The internal surface is fairly smooth, suggesting that the ethylene/propylene comonomers can diffuse into the subglobules readily and polymerize on the active centers inside. However, the macropores between the subglobules as observed in the iPP particle (Fig. 2(a)) are not totally occluded by the EPR. Some cavities are still observed (Fig. 5(a)), which may be caused by the ''pinch-off'' effect as McKenna et al. [17] described, where the preformed EPR might form the pinch-points in the pores and thus hinders the subsequent diffusion of the comonomers.

The distribution of EPR phase in the hiPP particle is verified by xylene extraction, which will remove EPR from the iPP matrix. Surface morphology of hiPP particle after solvent extraction (Fig. 6(a)) is similar to that of the iPP particle, and the smooth cross-section surface of hiPP subglobule becomes porous after extraction (Fig. 6(b)), confirming a finely distributed EPR within the subglobules.

Although the finely dispersed EPR phase in the hiPP particle is generally accepted, formation mechanism of the EPR is still in dispute. The main problem is focused on whether the EPR first forms on the active sites underneath the PP layer of the primary particle and then expands into the pores [15–17], or it forms on the catalyst fragments which are convected to the surface of the subglobules [18]. A detailed examination of the distribution of EPR within the hiPP particle is therefore needed. Fig. 7 shows BF electron micrograph of thin section of

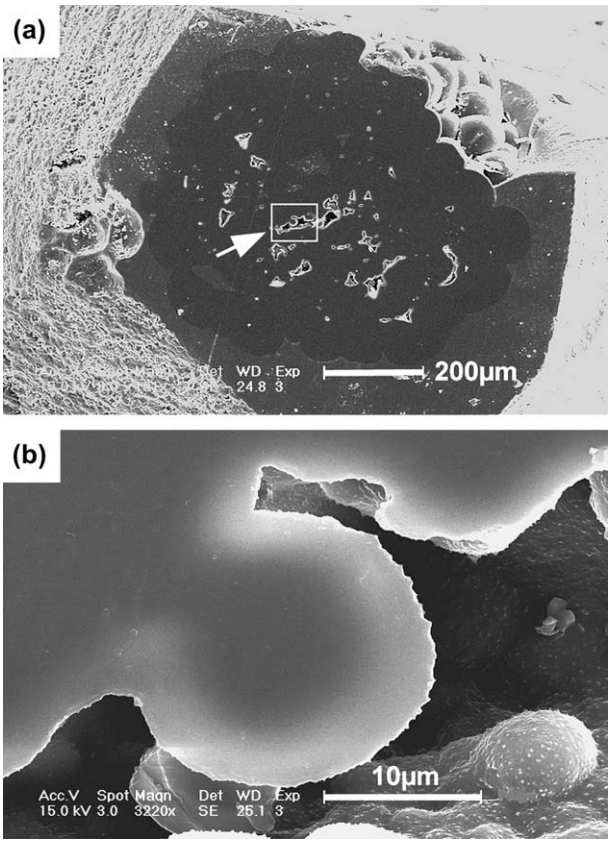

Fig. 5. (a) SEM micrographs of an overview of the cross-section of a hiPP particle; (b) as well as the internal surface of a subglobule, which is inside the hiPP particle as indicated by an arrow in (a).

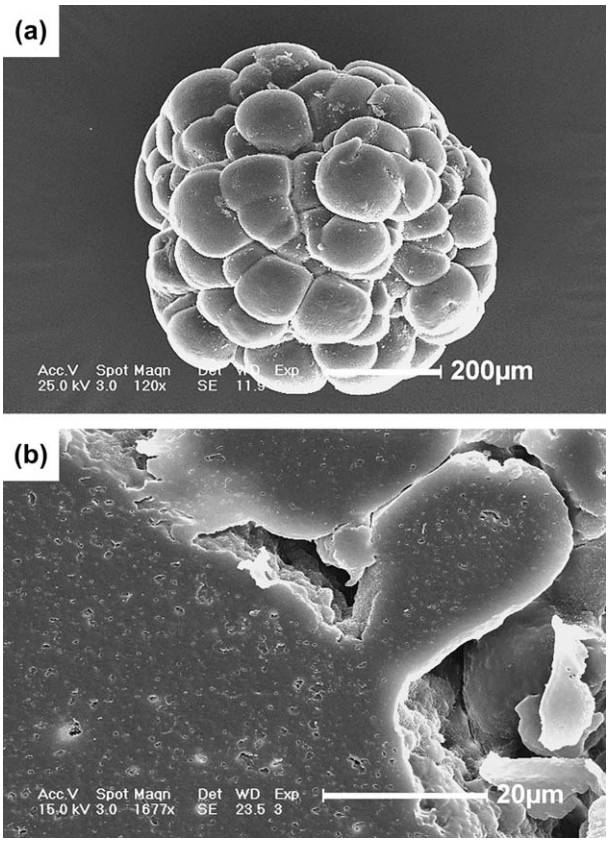

Fig. 6. (a) SEM micrographs of the external surface of a hiPP particle; (b) the cross-section of the hiPP subglobule after solvent extraction.

the hiPP subglobule after stained with RuO_4 for 4 h. Since the EPR phase will be stained readily than the semicrystalline polypropylene matrix at a short time of staining (ca. 4 h at 30 °C), it exhibits dispersed dark regions in Fig. 7. With a longer time of staining, the polypropylene matrix will be stained as well. As shown in Fig. 8, the thin section of hiPP particle was stained for 7 h at 30 °C. An agglomerate of EPR (as indicated by the arrow) with strong contrast and the surrounding matrix of polypropylene primary globules, which exhibits weak contrast compared with that of the EPR agglomerate, are displayed. Clearly, the morphology of polypropylene primary globules after copolymerization does not change compared with that of the iPP particle (Fig. 3(b)), and there is no sign that the EPR forms from the underneath of polypropylene primary globules and then flows out. Further evidence is presented in Fig. 9, where some larger agglomerates of EPR (as indicated by the arrows) are observed between the subglobules of hiPP, which are formed directly on the surface of the subglobules. These results suggest that the copolymerization takes place preferentially on the catalyst active centers which are located on the periphery of the micropores inside the subglobule and the macropores between the subglobules of iPP particle. The above observations are similar to that reported by Cecchin et al. [18], i.e., the EPR does not form on the active sites underneath the primary globule, but only on the catalyst fragments convected to the surface of the subglobules. However, the migration and surface accumulation of catalyst fragments within subglobules as they proposed are not observed in the present work. These dissimilarities might be

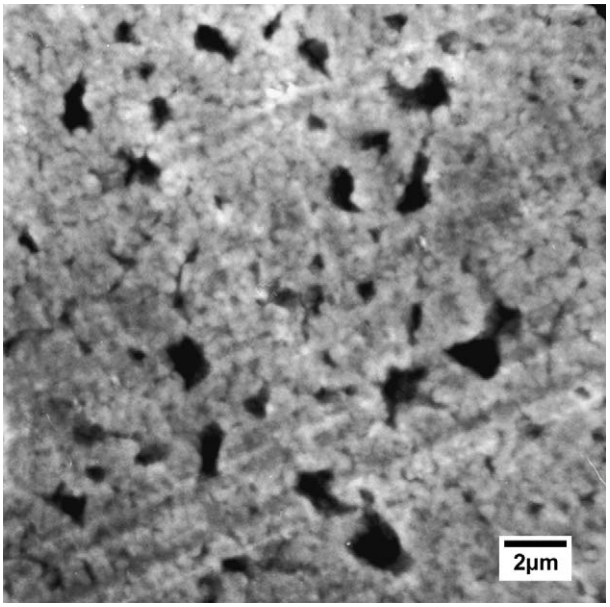

Fig. 7. BF electron micrograph of thin section of the hiPP subglobule after stained with RuO_4 for 4 h, showing the dispersed EPR phase in a polypropylene matrix.

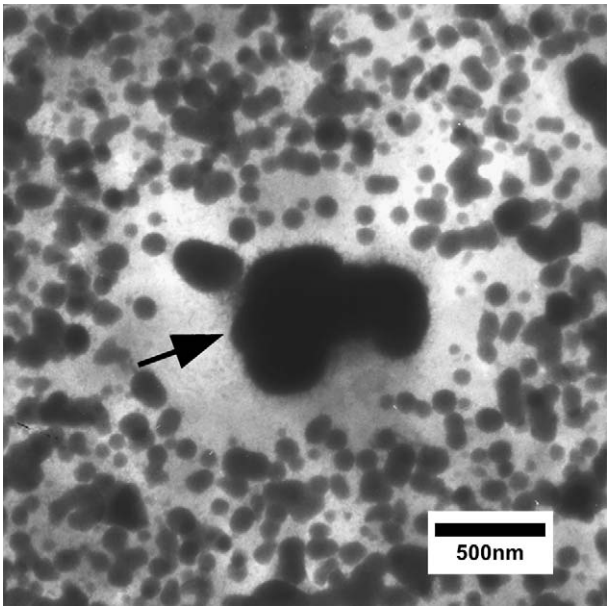

Fig. 8. BF electron micrograph of the thin section of hiPP subglobule after stained with RuO_4 for 7 h, showing an agglomerate of EPR (as indicated by the arrow) in a matrix of polypropylene primary globules.

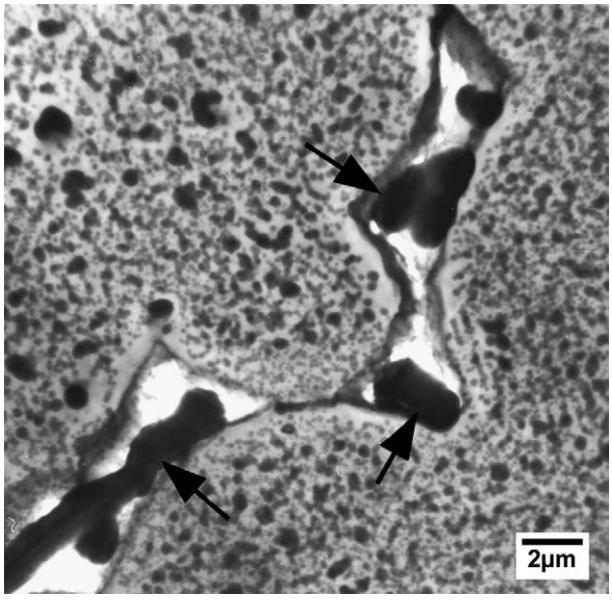

Fig. 9. BF electron micrograph of the thin section of hiPP particle after stained with RuO_4 for 7 h, showing some larger agglomerates of EPR (as indicated by the arrows) between the subglobules of hiPP.

attributed to the much smaller subglobules they observed. In addition, there should be a fine distribution of catalyst fragments within the iPP particle which are active for the copolymerization to occur. Therefore, formation and distribution of the EPR phase are mainly dictated by the accessibility of ethylene/propylene comonomers to these active centers, i.e., by the efficiency of the pore network of iPP particle.

4. Conclusions

From the morphological study of the iPP and hiPP particles produced in a multistage polymerization process, some general features about the construction of iPP particle and the distribution of elastomer phase in the particle can be obtained. The iPP particle exhibits a tertiary architecture consisting of many secondary subglobules with the diameter of ca. several to hundreds of microns. The subglobule in turn is formed by a great deal of primary globules ca. 100 nm in diameter. The large macropores between the subglobules and the finely distributed micropores within the subglobule constitute a network of pore inside the iPP particle. There is a fine distribution of catalyst fragments in the iPP particle, which are active for the copolymerization to occur. The ethylene/propylene comonomers can diffuse into the macro- and micropores and copolymerize on the catalyst active sites located on the periphery of the pores, forming the elastomer phase inside.

Acknowledgements

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References

[1] Simonazzi T, Cecchin G, Mazzullo S. Prog Polym Sci 1991;17:303.
[2] Galli P, Haylock JC. Prog Polym Sci 1991;17:443.
[3] Hutchinson RA, Chen CM, Ray WH. J Appl Polym Sci 1992;44:1389, and the references therein.
[4] Hock CW. J Polym Sci A1 1966;4:3055.
[5] Mackie P, Berger MN, Grieveson BM, Lawson D. J Polym Sci Polym Lett Ed 1967;5:493.
[6] Ferrero MA, Koffi E, Sommer R, Conner WC. J Polym Sci Part A Polym Chem 1992;30:2131.
[7] Ferrero MA, Sommer R, Spanne P, Jones KW, Curtis Conner W. J Polym Sci Part A Polym Chem 1993;31:2507.
[8] Noristi L, Marchetti E, Baruzzi G, Sgarzi P. J Polym Sci Part A Polym Chem 1994;32:3047.
[9] Bukatov GD, Zaikovskii VI, Zakharov VA, Kryukova GN, Fenelonov VB, Zagrafskaya RV. Polym Sci USSR 1982;24:599.
[10] Skomorokhov VB, Zakharov VA, Kirillov VA, Bukatov GD. Polym Sci USSR 1989;31:1420.
[11] Kakugo M, Sadatoshi H, Yokoyama M, Kojima K. Macromolecules 1989;22:547.
[12] Kakugo M, Sadatoshi H, Sakai J, Yokoyama M. Macromolecules 1989; 22:3182.
[13] Kakugo M, Sadatoshi H, Sakai J. Morphology of nascent polypropylene produced by $MgCl_2$ supported Ti catalysts. In: Keii T, Soga K, editors. Catalytic olefin polymerization. Tokyo: Kodansha-Elsevier; 1990.
[14] Urdampilleta I, Gonzalez A, Iruin JJ, de la Cal JC, Asua JM. Macromolecules 2005;38:2795.
[15] Debling JA, Ray WH. J Appl Polym Sci 2001;81:3085.
[16] Kittilsen P, McKenna TF. J Appl Polym Sci 2001;82:1047.
[17] McKenna TF, Bouzid D, Matsunami S, Sugano T. Polym React Eng 2003;11:187.
[18] Cecchin G, Marchetti E, Baruzzi G. Macromol Chem Phys 2001;202: 1987.