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A novel route to polyethylene–polystyrene blends through the fragmentation of porous polystyrene beads supported metallocene in ethylene polymerization†

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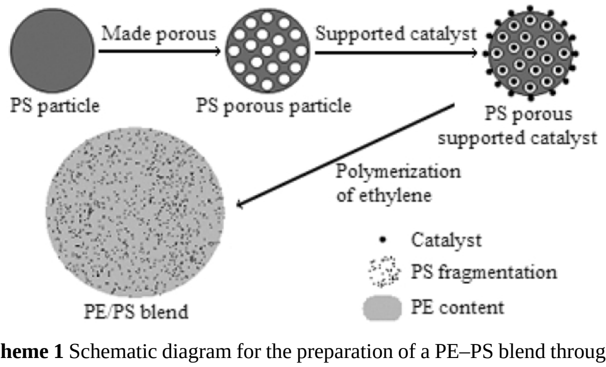
Polyethylene–polystyrene blends were synthesized by *in situ* ethylene polymerization with polystyrene porous beads supported metallocene; the influence of fragmenting support beads on the morphology and the mechanical performance of the blends was investigated.

Mixing different polymers to form polymer blends has become increasingly popular owing to the desire to produce materials at a lower cost, improve the performance of polymeric materials, and to enable the reuse of recycled industrial material.[1] Conventional methods for the preparation of polymer blends generally involves the addition of a compatibilizer, usually a block copolymer, or the introduction of reactive groups into one or more of the component polymers followed by reactive processing.[2,3] The compatibilizer and reactive groups can change the interfacial tension and adhesion between the phases, resulting in better compatibility.[4] However, conventional work on the blending of polymers has had limited success as the effects of interfacial agents on the morphologies and mechanical properties of the blends are very complex and good performance is not always obtained. On the other hand, it is known that morphology is very important to performance and only those blends with fine morphologies exhibit superior physical properties. Most polymers are, unfortunately, thermodynamically immiscible and it is difficult to mix them with fine particles, whose domain size is in the range of nanometers, by conventional methods. Recently, more effort has been directed towards the preparation of immiscible polymer blends with fine morphology by a route not involving a compatibilizer.[5–7]

In this communication, we attempt to develop a new route to the *in situ* synthesis of polyethylene–polystyrene (PE–PS) blends based on olefin polymerization with a supported catalyst, which is schematically presented in Scheme 1. By this route PS firstly acts as the support beads for the catalyst and ultimately disperses into the PE matrix as the support beads fragment during the polymerization of ethylene. It is known that catalyst particles break up into small fragments after polymerization and the fragments disperse into the polymer particles throughout the whole growth process when SiO_2 or $MgCl_2$ is used as the support for Ziegler–Natta catalysts.[8,9] In recent research of olefin polymerization with organic supported catalysts, we found that porous PS latex beads supported metallocenes also underwent fragmentation under certain conditions and this can be applied to the preparation of PE–PS blends. This approach allows nano-scale dispersion of PS into a PE matrix in the absence of a compatibilizer. In addition, this approach involves blending cross-linked PS and PE, which is difficult by other methods. In this work we focus on (1) the design of PS support particles and (2) the effects of support particle fragmentation on the morphology and mechanical performance of the blends.



Scheme 1 Schematic diagram for the preparation of a PE–PS blend through the dispersion of PS fragments into a PE matrix during ethylene polymerization.

To ensure a fine dispersion of PS in PE, the PS support particles were designed to be of small size and porous in structure to improve their ability to fragment. With this in mind, we employed emulsion polymerization to produce PS support particles and treatment stepwise with alkali and acid to make the support particles porous.[10] The PS particles were mostly composed of styrene with a little ethyl acrylate, acrylic acid and divinylbenzene (DVB); the acid groups helped to make the latex particles porous in the alkali and acid treatment, the carbonyl groups served as the connection between the catalyst and the support in the next treatment with metallocene, and DVB was used as the crosslinker. The size of the PS particle was about 300 nm in diameter and the porosity of the support was confirmed by transmission electron microscopy (TEM). Such porous supports have a high surface area in the dry state, typically in the range of 750–800 $m^2\ g^{-1}$ measured by N_2 sorption and application of the BET (Brunauer–Emmett–Teller) theory.

Subsequently, the porous PS particles obtained were used for supporting the metallocene catalyst. In the experiment Cp_2ZrCl_2 was used as the metallocene and toluene as the solvent. The support was firstly mixed with a solution of methylaluminoxane (MAO) for 3 hours to remove traces of water and next with a solution of Cp_2ZrCl_2 for 5 hours to immobilize the metallocene. After removal of the residual metallocene the supported catalyst was dried *in vacuo* until a fine solid powder was obtained. The porous supported catalyst so obtained could be used for the polymerization of ethylene.

Lastly, the PE–PS blend was fabricated by the polymerization of ethylene using the porous PS supported catalyst. As an example, polymerization of ethylene was performed using the PS supported catalyst and MAO as the cocatalyst at 60 °C with 1.2 bar ethylene pressure in a toluene solvent. After the required reaction time the resulting mixture was quenched with ethanol, filtered, washed and dried. The PE–PS blend was obtained as a white solid. It should be mentioned that by controlling the polymerization conditions, such as the reaction time or the dose of supported catalyst, the amount of PS incorporated into the PE substrates can be conveniently adjusted to various values.

The morphology of the PE–PS blend obtained was investigated by observing the distribution of PS in PE by TEM. Prior to examination, ultrathin sections of the PE–PS blends were cut using an ultramicrotome and these were chemically stained in RuO_4 vapor for 24 h. The TEM micrographs of the blends with different PS contents are presented in Fig. 1, in which the RuO_4-stained PS appears as dark areas. Fig. 1 shows that the PS component is

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distributed homogeneously in the PE matrix and that the PS domain size is very small (Fig. 1a). Such a homogeneous distribution arises because the PS support particles disintegrate gradually as the polymerization proceeds and pieces of PS disperse into the PE product. It is evident that polymerization takes place not only on the surface but also inside the interior of the support particle and the growing polyethylene swells the particle, breaking up the particle. However, the size of PS phase will increase with increasing PS content in the blend (Fig. 1b). It is also noted that despite the absence of compatibilizing agents, PE and PS are quite compatible with each other in the blend, and it can be seen from Fig. 1 that the phase boundary between the PE and PS phases is not clearly defined. We believe that the interphase compatibility will enhance the interface adhesion, which also contributes to the improvement of the mechanical performance of the blends.

It is clear that the key factor in the synthesis of PE–PS blends with fine phase size is the fragmentation of the PS support particles during ethylene polymerization. With this in mind we tested solid PS particles as support for the catalyst, which were also prepared by emulsion polymerization but without the alkali and acid treatment. The result was that the blend obtained *via* ethylene polymerization with a solid supported catalyst was unacceptable, exhibiting coarse phase morphologies as shown in Fig. 2a, with the PS particles remaining in the PE matrix. It is evident that the solid support particles had poor fragmentation ability or even hindered fragmentation during ethylene polymerization. On the other hand, the fragmenting efficiency of support beads also depends on the ethylene polymerization conditions, such as polymerization temperature and time. Our results showed that when the polymerization was carried out at a lower temperature (40 °C) and with less MAO, the porous support particles did not fragment completely (Fig. 2b) due to insufficient activity of the catalyst ($\sim 2 \times 10^5$g polymer (mol Zr)$^{-1}$ h^{-1} bar^{-1}).

Up to now much literature has described PS or modified PS beads as catalyst carriers for olefin polymerizations and the fragmentation of the support particles has been addressed in some cases.[11] However, the feasibility of synthesizing polymer blends through ethylene polymerization with supported catalysts had not been investigated. Moreover, the PS supported catalyst systems described in the literature were not necessarily applicable to the synthesis of polymer blends because of the difficulties in achieving fine fragmentation of supports due to the large size of support particles (usually 50–100 μm). The lack of information about the distribution of the support in polyolefins also made the investigation into blend morphology impracticable. It is seen from our experiments that by making small and porous PS beads, we can improve the fragmentation ability of support particles and achieve the dispersion of fine PS pieces in the PE component, thus synthesizing blends with superior properties.

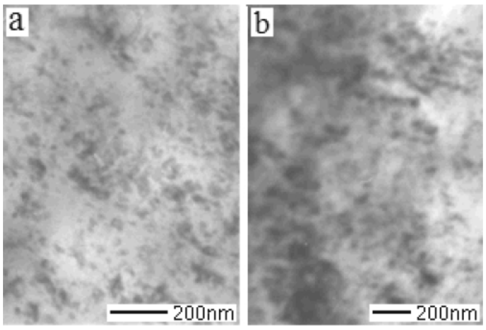

Fig. 1 TEM micrographs of PE–PS blends obtained with different PS contents: (a) 4 wt% PS and (b) 16 wt% PS.

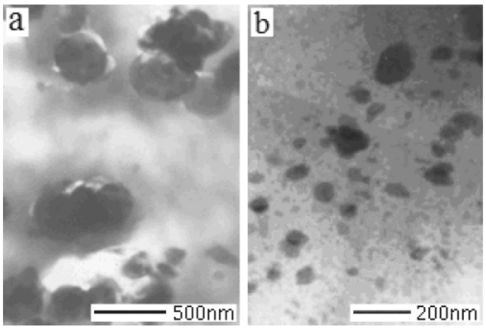

Fig. 2 TEM micrographs of PE–PS blends with (a) unfragmented PS beads and (b) partially fragmented PS beads.

As one might expect, mechanical properties were improved significantly by blending PS and PE with fine morphology. For example, when the molecular weights of PEs were at the same level, the Young's modulus of the PE–PS blend with 4 wt% PS (825 MPa) was reasonably higher than that of pure PE produced with the homogeneous Cp_2ZrCl_2 catalyst (550 MPa). However, the improvements in Young's modulus with blends from partially fragmented PS beads dispersed in the PE matrix (typically in the range of 580–660 MPa) were quite limited due to the somewhat coarse phase morphologies, whereas those PE–PS blends with unfragmented PS beads exhibited poor mechanical properties. It thus can be concluded that total fragmentation of the PS support and the fine PS phase morphology in PE is an essential factor in improving the mechanical properties of blends.

In summary, our preliminary experiments have proved that the disintegration of the support during ethylene polymerization with porous PS particles supported catalyst is a novel approach towards *in situ* synthesis of PE–PS blends with fine morphology. This strategy is versatile and should be applicable to the synthesis of different kinds of polymer blends, such as PE–PMMA, PP–PS, PP–PMMA, depending on the components of the supports and monomers. The main advantage of our procedure is that once the supported catalyst has been developed the blending of polymers can be done with ease using existing olefin polymerization equipment, providing a direct means to lower costs relative to classical blending methods.

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