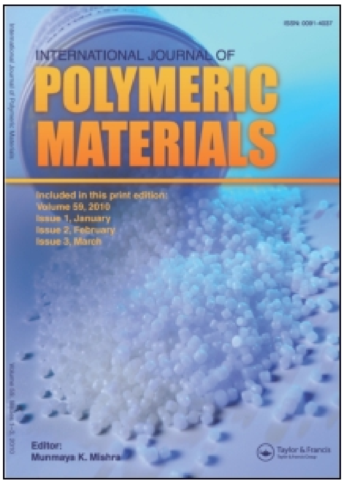

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Core-shell Nanoparticles Reinforced Polystyrene with no Effect on its Transparency

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Core-shell Nanoparticles Reinforced Polystyrene with no Effect on its Transparency

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Bisvinyl-A and styrene core-shell copolymer nanoparticles with different particle size were synthesized through the composite emulsion polymerization. The PS (polystyrene) blends with different concentration and particle size of core-shell nanoparticles were prepared. The impact strength and the transparency were studied which indicated that the best condition for reinforced the PS was that the particle size was above 100 nm and the concentration of the particles in PS blends was roughly within the range of 2 ~ 5% weight percent, which improved the strength of PS near to two times while the PS transparency was not affected.

Keywords: Polystyrene; blends; core-shell nanoparticle; UV spectra; transparency; impact strength

1. INTRODUCTION

Two-phase polymer systems have become important items of commerce. Blends of plastics is a well known phenomenon used to improve the mechanic properties. The mechanical behavior of blends composed of grafted rubbery particles and brittle polymer, such as PS and styrene acrylonitrile (SAN), has been the subject of intensive research [1–3]. The improved toughness of high impact PS and acrylonitrile butadiene styrene (ABS) is thought to be caused by grafted polybutadiene particles acting as both craze initiators and terminators.

The PS with high transparency as commercial product was widely used, however, the use was limited due to its drawback which is brittle and of low impact strength. In order to improve its impact strength while there is no effect on its transparency, the choice of the dispersed-phase material is of importance. Even though the individual phase may be transparent, a normal drawback of this class of materials is their lack of transparency caused by the scattering of light at the interface between the phases. It has long been known qualitatively that two-phase systems could be made transparent by reducing the dispersed-phase particle size and/or by matching the refractive indexes of the phase [4].

In this paper, we chose bisvinyl-A(1a) and styrene as monomer to prepare the micro-crosslinked core-shell copolymer nanoparticles to modify the PS according to the principles mentioned above. The impact strength of PS blend was studied and the transparency was measured by UV spectra, which indicated that the core-shell nanoparticles can reinforce the PS with no effect on its transparency within some range of the particle size.

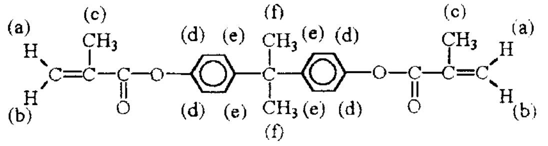
2. EXPERIMENTAL

$K_2S_2O_8$, sodium oleate (so), chloroform, toluene, and methanol used in the present work were all analytical grade agents; Styrene (technical grade) was distilled under reduced pressure. The synthesis of Bisvinyl-A was similar to reference [5]. Table I summarized the H chemical shifts of bisvinyl-A determined by ^1H NMR, which indicates that the structure of bisvinyl-A is as (1a).

TABLE I H chemcial shifts of bisvinyl-A measured by ^1H NMR

H position	*a*	*b*	*c*	*d*	*e*	*f*
Chemical shifts (ppm)	5.75	6.33	2.05	7.06	7.00	1.69

a, b, c, d, e, f represent the H position of bisvinyl-A.



(1a) Bisvinyl-A

Structure (1a) bisvinyl-A structure

The core-shell nanoparticles were prepared by composite emulsion polymerization. Firstly, the sodium oleate and distilled water were charged to a 3-necked glass flask followed by bisvinyl-A and one half of the styrene mixture. The reaction vessel was then placed in an oil bath at 90 °C and the mixture was stirred under the N_2 atmosphere. The $K_2S_2O_8$ was added to polymerize for 1 hour. Secondly, the remainder of styrene was added dropwise over 2 hours. The reaction was held at 80 °C for additional 1 hour.

A small amount of emulsion was diluted in distilled water, then a drop of this solution was dripped onto a copper grid to examine the surface morphology and the particle size by TEM. The remainder of the emulsion was precipitated by methanol and dried under 60 °C for 48 hours.

The various compositions of PS/C-S (core-shell particles) were compounded at varied weight ratio, and then they were blended in the Brabender single Screw Extruder at 200 °C, 60 rpm. The impact strength experiments were done.

The mixtures with varied weight ratio of PS/C-S were dissolved in toluene and chloroform mixed solution (volume ratio 1:1) respectively, then they were poured onto the mercury surface to form the casting films for UV spectra measurement.

3. RESULTS AND DISCUSSION

The core of the core-shell nanoparticles was mainly formed at the first stage for composite emulsion polymerization. So the weight ratio of the monomer (W_m) and the emulsifier (W_{SO}) is of importance to control the core-shell particle size and its structure without changing other parameters. According to this, we designed different weight ratio of monomer and emulsifier to synthesize the microgel core-shell nanoparticles with different particle size. Figure 1 showed that it was a good linear relationship between particle size and W_m/W_{SO} which coincided with the Fitch's theory [6]. From this figure, we can also find that the plotted function shows that at this condition of polymerization, the smallest particle size we can obtain was not less that 25 nm to adjust W_m/W_{SO} value. Therefore, we can prepare the particles from 50 to 150 nm with narrow size distribution to coordinate some factors

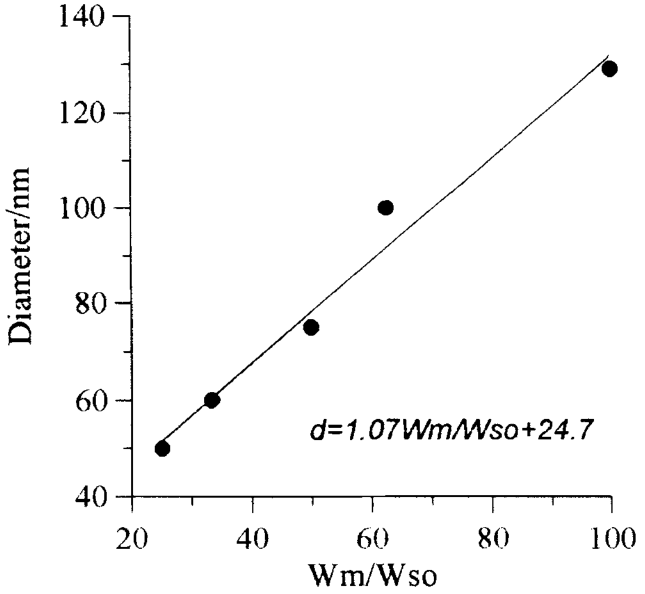


FIGURE 1 Relationship between the particle size and W_m/W_{so}.

such as W_m/W_{SO}, the concentration of the initiator and temperature etc.

Figure 2 was the TEM photograph of core-shell nanoparticles. Because the core is crosslinked, its density is much higher than that of the shell. So that we can observe the core-shell structures of the particles, and we also find that the particle size distribution is very narrow (Fig. 3). Its polydispersity is just only 1.004 calculated according to the following equation.

$$Q = \sum n_i D_i^2 \quad \left(\sum n_i D_i\right)^2 \tag{1}$$

where, Q is the polydispersity of particles n_i is the fraction of the particles whose particle size is D_i.

As the impact strength of core-shell particles is much higher than that of the PS, the enhancement of the impact strength of the blend of the PS with particles is expected. From Figure 4, we can find that the impact strength of the PS blend varies with the content of the

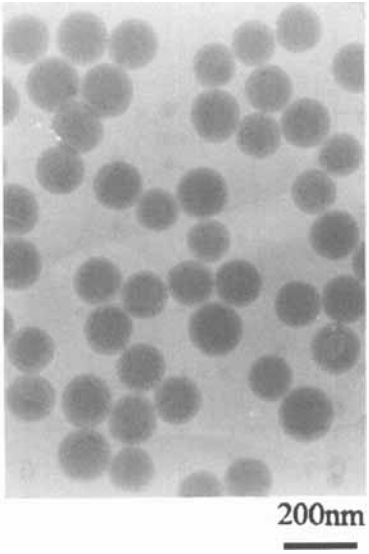


FIGURE 2 TEM micrograph (× 50 K) of the core-shell particles.

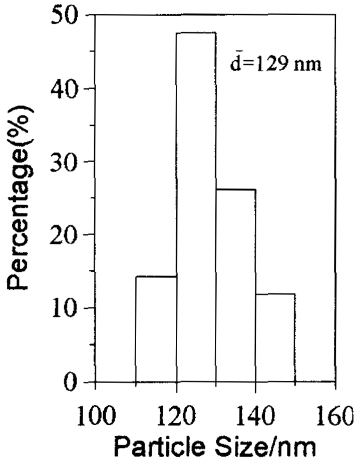


FIGURE 3 Size histogram of the core-shell particles shown in Figure 2.

core-shell particles, and they all have maximums when the weight percents of dispersed-phase in blend are between 2～5%. From this figure, we also find that it has different effect on the impact strength for the core-shell particles which have different average particle size.

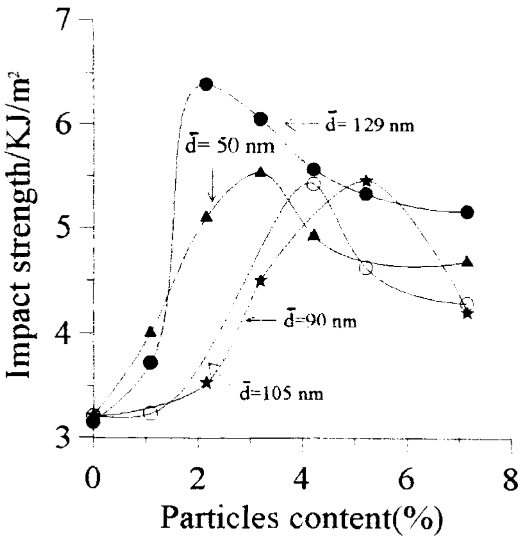


FIGURE 4 Relationship between the impact strength of PS C-S blends and C-S content with different average particle size.

Compared with the four curves, the biggest enhancement of the impact strength is over 200% for the particles whose average diameter is about 129 nm, which indicates that the dispersed-phase particle size is a main factor to affect the impact strength, only if the dispersed-phase size exceeds a certain value (100 nm), the impact strength can improve sharply.

In order to improve the impact strength of the PS without effect on its transparency, the two factors should be concerned. One is the dispersed-phase particle size, the other is the matching of diffractive indexes of the two kinds of materials. In general, the impact strength of the blend will increase with the dispersed-phase particle size, however, the excessive particle size will cause the big distance between the particles so that the particles will not terminate the craze of the system effectively. Thinking the influence on the optical properties of the materials, we can find that the biggest particle size should be less than 200 nm according to the reference [7]. For the matching of the diffractive indexes of the two phases, the diffractive index of the core-shell particles used here is 1.589 which matches well with that of the PS. As the shell of the particles was made of styrene which can improve the

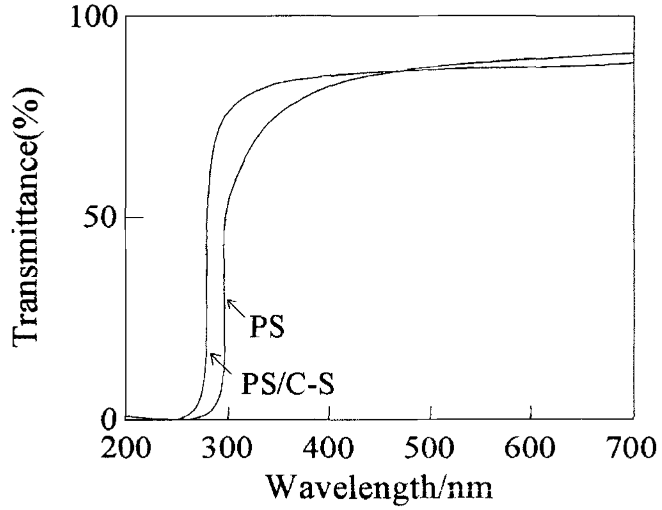


FIGURE 5 UV spectra of PS and PS/C-S blend. The average particle size of C-S is 129 nm, and *Wc-s*/*Wps* = 8%.

compatibility of the particles and PS, the core-shell particles can easily disperse well into the PS matrices. So the UV spectra (Fig. 5) shows that there is hardly effect on the transparency of PS for the blend of PS with core-shell particles.

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