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LETTER

Study of nanocomposites containing core-shell fillers with rigid nano-SiO_2 core in PMMA matrix

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Through the years the subject of polymer toughening has attracted attention from both academia and industry. An effective method to toughen inherently brittle polymers is rubber toughening [1–4]. While the incorporation of rubber particles can improve the fracture toughness in brittle polymers, it will also reduce the tensile modulus and tensile strength accordingly [1]. From an application view point, one would naturally prefer to have materials that are tough and with the tensile properties maintained. The natural choice would be the incorporation of rigid fillers (such as inorganic particulates or glass fibres) and soft elastomeric inclusions simultaneously [5–7]. The reinforcement theories of fibre reinforced composites are well documented [8]. In our earlier studies [5] on short glass fibre (SGF) and rubber (an EPR rubber) filled polypropylene (PP) ternary blends, both SGF and rubber inclusion improved the impact fracture toughness of brittle PP homopolymer. However, the ability of SGF to toughen the PP matrix is well below that of the elastomer.

In recent years, studies on nanosize rigid particles modified polymer matrix composites have demonstrated that dramatic properties' improvement can be achieved with only a low level of fillers added [9–11]. Ou et al. [9] showed that with the addition of 5 wt% of silica particles (with sizes ranging from 50 to 110 nm) in nylon 6, the tensile modulus, tensile strength, elongation at break and impact strength have all been significantly improved. Nowadays, the preparations of organic/inorganic nanoparticles with core-shell structures through both emulsion [12–15] and dispersion polymerization [16] have gained much progress. However study of the characteristics of these nanoparticles in polymer matrix as functional fillers is still rare [17–19]. In this article, we will report on the preparation of core-shell nanoparticles with rigid SiO_2 core and rubbery polybutyl acrylate (PBA) shell via in situ emulsion polymerization and its application as toughening filler of PMMA through emulsion co-precipitation method.

Silica nanoparticles with size of ~40 nm (grade D-60287) was supplied by Degussa (China) Co. Ltd. and were used after drying in vacuum at 105 °C for 12 h. The pre-treatment of silica with vinyltriethoxysilane (VETOS) was carried out using a previously published procedure [19]. The monomers, methyl methacrylate (MMA) (from Tianjin Boyou Chemical Co. Ltd.) and butyl acrylate (BA) (from Tianjin Comile Chemical Agent Co. Ltd.) were distilled under reduced pressure before use. The initiator, ammonium persulphate (APS), was recrystallized from water before use. The surfactant, sodium dodecylsulphonate (SDS); the demulsifier, $AlCl_3$; and the buffering agent, $NaHCO_3$ were used without further purification. The crosslinking agent 1,3-butanediol dimethacrylate (BDMA) was supplied by Tokyokasei (TCI) Co. Ltd. and used as received.

The emulsion polymerization was carried out in a 250 ml four-necked round-bottomed flask, which was equipped with a reflux condenser, a mechanical stirrer, a dropping funnel and a nitrogen gas inlet, respectively. In a typical synthesis, the modified nano-SiO_2 powder was dispersed into distilled water with the aid of ultrasound bath for 2 h. The initiator (APS) was dissolved in a definite amount of distilled water, and then the buffer solution of $NaHCO_3$ and surfactant (SDS) was added. This solution

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was transferred into the reactor flask, which was charged with modified nano-SiO$_2$ dispersion. The initial charge was stirred at 300 rpm for 2 h before feeding with monomers. Afterward, the monomers (BA or BA/BDMA mixture) were fed into the reactor in a separate stream with constant flow rates which were slow enough to reach monomer-starved conditions. The time of feeding was 60 min and after addition of the monomers, the content was heated up to 75 °C and stirred for an additional 4 h. Then, the system was cooled to room temperature and the final latex was obtained. The latex with nano-SiO$_2$ particles was then mixed with a certain amount of pure PMMA latex (formulation refer to Latex 4 in Table 1) under constant stirring. Then the mixed latex was subjected to demulsification with AlCl$_3$ solutions, and the product was collected by suction filtration and washed thoroughly with hot water, then dried. The detailed recipes prepared in this research are given in Table 1. Basically, latexes 1, 2, 3 and 4 were first produced. Subsequently, latex 4 was mixed with latex 1, 2 and 3 to obtain blends 5, 6 and 7, respectively.

Figure 1a, b shows the TEM micrographs of Latex 2 and Latex 3, respectively. It was found that the micelles in Latex 2 without the crosslinking agent (BDMA) had relatively larger particle size than those in Latex 3 with BDMA. This was because the micelles with uncrosslinked shell are much softer than those with crosslinked ones. These uncrosslinked micelles will be deformed and flattened more easily on the copper grid when the TEM samples were prepared. And it can be clearly found in the micrograph of Latex 2 that not single but SiO$_2$ particle clusters were encapsulated in the individual micelle. This result is similar to other reported works [12].

Table 1 Emulsion formulation of SiO$_2$-PBA core-shell rubber and SiO$_2$-PBA/PMMA blends

Latex

Sample	BA (g)	NaHCO$_3$ (mg)	APS (mg)	SDS (g)	SiO$_2$ (g)	BDMA (mg)
Latex 1	3	8	10	0.1	0	0
Latex 2	2.1	8	10	0.1	0.9	0
Latex 3	2.1	8	10	0.1	0.9	4.2

	MMA (g)	NaHCO$_3$ (mg)	APS (mg)	SDS (g)	SiO$_2$ (mg)
Latex 4	3	8	10	0.1	0

Blend

Blend 5[a]	Latex 1 + Latex 4
Blend 6[b]	Latex 2 + Latex 4
Blend 7[c]	Latex 3 + Latex 4

[a] The weight ratio between PBA and PMMA is 1:9; [b] The weight ratio of PBA + SiO$_2$ and PMMA is 1:9; [c] The weight ratio of PBA + SiO$_2$ and PMMA is 1:9

Figure 2 is the DSC heating curve of pure PMMA (obtained from Latex 4) and the PMMA blends with different kinds of fillers. It could be found that for pure PMMA, the glass transition temperature (Tg) is around ~114 °C. When added with pure PBA rubber (Blend 5), the Tg value decreased to ~103 °C because of the low Tg of PBA (~−76 °C) [20, 21]. While adding core-shell particle with SiO$_2$ core and PBA shell in PMMA matrix (Blend 6), the Tg of PMMA again increases to ~108 °C. The Tg increase is due to SiO$_2$ core acting as entanglement points of the PBA shell which will strongly prohibit the movement of the PBA molecular chains and increase the Tg of PBA. Furthermore, when the PBA shell was crosslinked with BDMA in which the PBA molecular chain will be further restricted and results in further Tg increased of the rubber shell, as well as the Tg of PMMA blends (~115 °C) (Blend 7).

The storage modulus (E′) versus temperature plots for pure PMMA and the different blends are compared in Fig. 3. It can be found that the storage moduli of blends with core-shell fillers (Blend 6 and Blend 7) are significantly higher than those with only pure rubber toughener system (Blend 5). When the temperature is lower than the Tg of PBA, the storage moduli of blends with core-shell toughener (Blend 6 and Blend 7) are even higher than that of pure PMMA. This is due to the combined reinforcement effects of the glassy rubber shell and rigid SiO$_2$ core of the core-shell fillers. When the temperature exceeds the Tg of PBA, the storage moduli of these blends decreased rapidly and finally become lower than that of pure PMMA. Comparing the two blend systems with core-shell fillers, the storage modulus of the one with crosslinked PBA shell (Blend 7) is slightly higher than that with uncrosslinked PBA shell particles (Blend 6) within the whole temperature zone.

The TGA results shown in Fig. 4 show that the thermal stability of blend with cross-linked core shell particles (Blend 7) is also higher than that with uncrosslinked ones (Blend 6). These results indicated that the crosslinking of rubber shell of core-shell particles will enhance not only its modulus but also its thermal stability.

In summary, core-shell particles with rigid SiO$_2$ core and rubbery PBA shell have been prepared through in situ emulsion polymerization method, and these core-shell particles were incorporated into PMMA matrix. The existence of rigid SiO$_2$ core in the core-shell particles can dramatically enhance the modulus of the blends compared to the addition of pure PBA rubber particles alone. The crosslinking of the rubber PBA shell of the core-shell particles does not only improve the modulus but also the thermal stability of the blends.

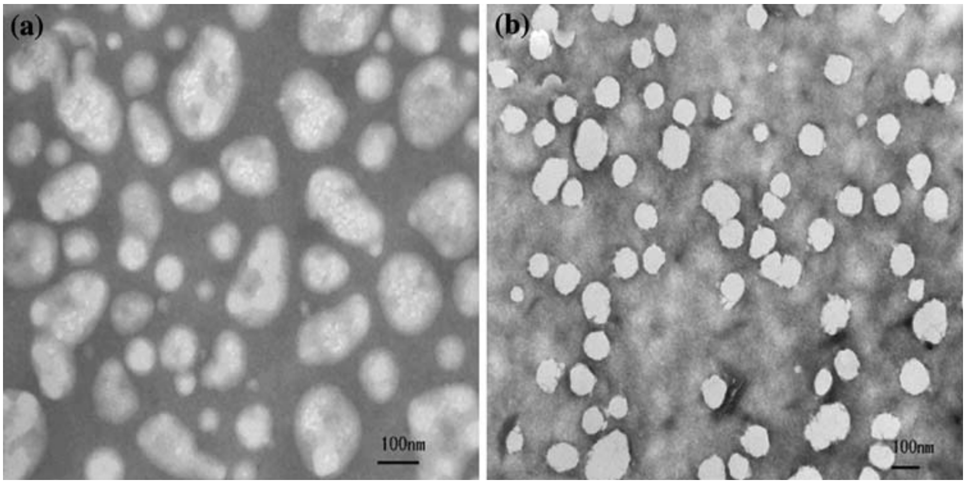

Fig. 1 TEM photograph of core-shell PBA/SiO$_2$ micelles: (**a**) with BDMA (Latex 2); and (**b**) without BDMA (Latex 3)

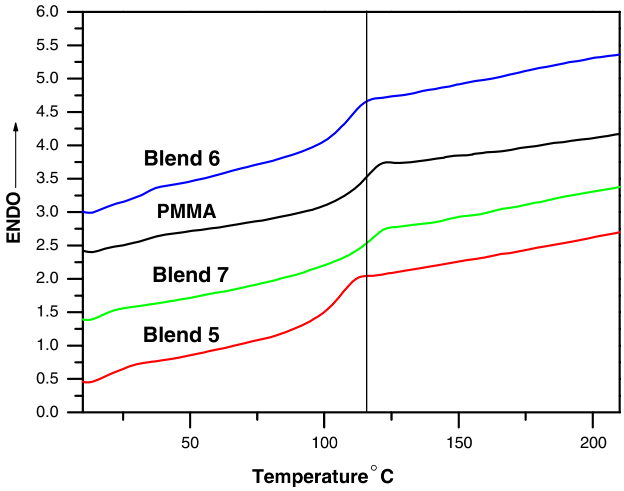

Fig. 2 DSC heating curves of PMMA and the different blends

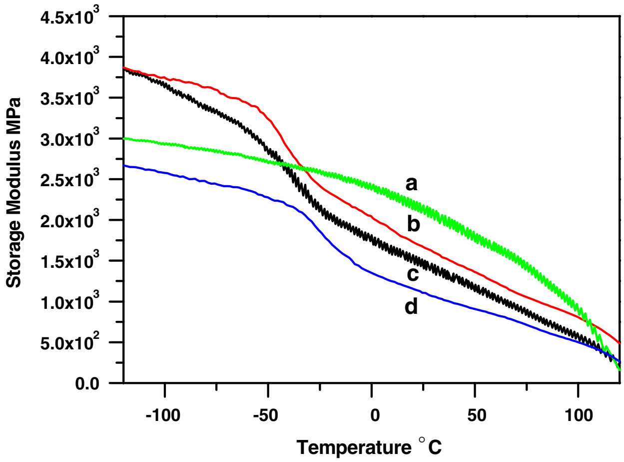

Fig. 3 Effect of temperature on the storage modulus for: (**a**) Pure PMMA; (**b**) Blend 7; (**c**) Blend 6; and (**d**) Blend 5

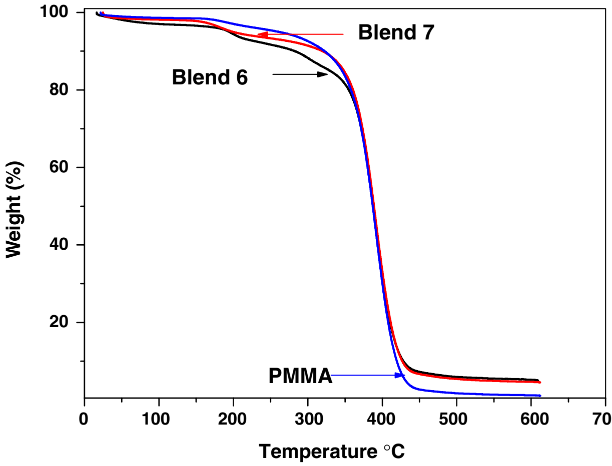

Fig. 4 TGA results of PMMA nanocomposites with core-shell particles

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