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Properties of rubber-toughened Polyvinyl chloride blends based on core-shell modifier with different particle morphology

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Summary

An analysis was made on the effects of particle morphology on the mechanical and optical properties of polyvinyl chloride/methyl methacrylate-butadiene-styrene (PVC/MBS) blends. Special care was taken to make comparisons of blends with different structural MBS under same conditions. The blend with a three-layer structure MBS had a lowest brittle-ductile transition (BDT) temperature, while the blend with a two-layer structure MBS had a relatively higher BDT temperature due to its higher Tg of rubber particles enhanced by combination of St. Furthermore, the transparency of blend with two-layer structure MBS was higher than that with three-layer structure MBS. In addition, SEM investigations showed the cavitation of rubber particles took place to remove the plastic constraint and promote a large volume of deformation in the blend with three-layer structure MBS.

Keywords: core-shell modifier; MBS; morphology; blends

Introduction

A well-established means to improve the toughness of brittle polymer is to incorporate a dispersed rubber phase in order to improve the impact strength [1]. Core-shell modifiers can toughen polymer matrix more effectively and are widely used in PC, PMMA, PVC and SAN [2-5]. As to core-shell modifier, the particle size, which is set during the synthesis process, can remain after they are dispersed in a host matrix and the shell of modifier functions as the layer that physically binds the matrix to the rubber core.

In common, core-shell modifier can be synthesized by emulsion polymerization. Modern polymerization methods have led to the possibility of preparing core-shell modifiers with a range of different particle size and desired morphologies. Many of the emulsion polymerization process parameters: hydrophilicity of monomer, the addition sequence of monomer, the initiate type, which are varied to prepare the toughened particles, have an influence on the particle morphologies [6-10].

It is well known that the morphology of the toughening rubber particles has a large influence on the physical and mechanical behavior of the resulting toughening matrix [11]. Much research indicated that the changing of the internal structure of the modifier might affect the subsequent toughened deformation of its host matrix. Schneider et.al [12, 13] have focused on the toughening of PS by the natural rubber based particles. They pointed that the core-shell particles based on NR containing a large number of PS subinclusions toughened PS most effectively. Pearson et.al [14] found that compared with rubber particles with two-layer structure the core-shell particles with three-layer structure can toughen PMMA matrix effectively. Plummer et al [15] have focused on the effect of the particle morphology on deformation in rubber modified PMMA. They also pointed out that the particles with two-layer and three-layer structure deformed via different way.

In our previous paper, the effects of St arrangement in MBS on the properties of PVC/ MBS blends were investigated. It was found that the changing of structure of MBS led to different deformation behavior [16]. In this paper, two type MBS with different internal structure were used as modifiers: (i) two-layer (2L)core-shell particles with a homogenous SBR core and PMMA, PS shell;(ii) three-layer (3L) particles with a styrene-rich SBR core, surrounded by an inner butadiene-rich shell of SBR and finally an outer shell of PMMA and PS. The mechanical and optical properties of PVC/MBS blends were investigated.

Experimental

Materials

MBS core-shell modifier was synthesized in two steps by emulsion polymerization: the synthesizing of SBR seed latex firstly and then grafting methyl methacrylate(MMA) and styrene(St) onto SBR seed latex. In the process of preparing SBR, water-soluble $K_2S_2O_8$ was used as initiator, and a mixer of rosin and fatty acid (FAD) was used as emulsifier. As to the seed latex of MBS with two-layer structure was synthesized, the DI water, the initiator, emulsifier, butadiene(Bd) and St monomer were added into a stainless steel reactor simultaneously, and the react was carried at 65°C for 25 h. When the seed latex of MBS with three-layer structure was synthesized, the DI water, the initiator, emulsifier, a small part of butadiene and a large part of styrene monomer were added into a stainless reactor to react first for 10 h to form a relatively hard core. And then the residual monomers were added with additional emulsifier and initiator to the system to continue polymerizing for 15 h to form SBR with hard-core and soft-shell. Finally, St and MMA were grafted on the SBR seeds to form the grafted layer. During the grafting process, an oil-soluble initiator, cumene hydro-peroxide (CHP), was used in combination with a redox system. The redox initiator system, sodium pyrophosphate (SPP), dextrose (DX) and iron (II) sulfate (FeSO4) was used without further purification. The emulsion polymerization was performed in a 1 L glass reactor under nitrogen at 70°C, and the reaction took place in an alkaline condition at PH10. When the reaction was completed, the polymers were isolated from the emulsion by coagulation and dried in a vacuum oven at 50°C for 24 h before used. So the MBS with two-layer and three layer structure were obtained.

Table 1 gave the characteristics of MBS core-shell modifier. And the scheme of structure of MBS was shown in Figure1. MBS1 have a two-layer structure with a homogenous SBR core and PS, PMMA shell while MBS2, MBS3 have a three-layer structure with St-rich SBR core, surrounded by a Bd-rich inner layer and finally an outer shell of PS and PMMA.

PVC resin, which has a K value of 66, was supplied by Jilin Chemical Company, China. M_w and M_n for PVC resin are 72,000g/mol and 40,000g/mol, respectively.

Table 1 The characteristics of the core–shell MBS particles used in this study

Sample	M/B/S in the core-shell particle	Structure of MBS	Total Bd/St in the core	Bd/St in the inter-core	Bd/St in the middle-layer	Particle size of core of MBS µm
MBS1	30/42/28	2L	75/25	–	–	0.121
MBS2	30/42/28	3L	75/25	50/50	91.6/8.4	0.118
MBS3	30/42/28	3L	75/25	33/67	93/7	0.120

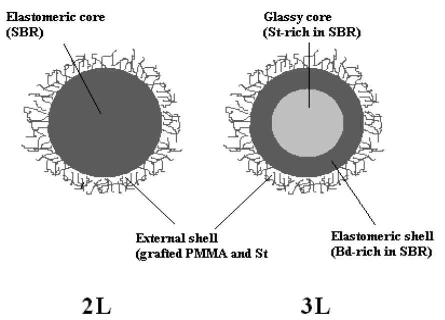


Figure 1 Schematic representation of the MBS morphologies: 2L, soft-core/hard-shell particles; 3L, hard-core/soft-inner layer/hard-shell particles.

Blend preparation

Blends of PVC, MBS, heat stabilizer and lubricant were compounded by roll-milling at 165°C for 5min. In all the blends, the MBS content was kept at the same level of 15wt%. The films obtained were then pressed into sheets by compression molding at 186°C for 10 min. The sheet thickness was set at 1 mm for the transparency tests and tensile test and at 5 mm for the Izod impact tests.

Dynamic mechanical thermal analysis

The tanδ of MBS core-shell modifier was measured on the DMA242 (Dynamic Mechanical Analyzer) at a frequency of 10 Hz and a heating rate of 3°C/min with the temperature range -120°C to 120°C. A plot of tanδ was recorded as a function of temperature. The Tg was taken as the temperature of the maximum in tanδ plots. Measurements of all the samples were made at identical conditions.

Mechanical properties

The notched Izod impact strength was determined according to ASTM D-256. The impact speed was 3.46ms^{-1}; the energy of the hammer was 10.8J. Specimens

($63.5\times12.7\times5mm^3$) were cut from the compression-molded sheet. The notch was milled in having a depth of 2.54mm, an angle of 45° and a notch radius of 0.25 mm. A series of impact tests were carried out at different temperatures ranging from -25°C to 25°C to show the brittle-ductile transition for each blends. The Izod impact strength was an average of five measurements per sample at each temperature.

All tensile specimens were molded into dumb-bell type whose dimensions of the parallel part were 60mm in length with a cross-section of about 12.90×2.90 mm^2. Tensile tests were conducted on AGS-H 5kN Electrical Testing Machine at constant cross-head speed of 50mm/min at 23°C according to ASTM D638.

Optical and stress whitening properties

Transmittances of blends were measured by using a Spherical Hazemeter (WGW) at 23°C according to ASTM D1003. The specimens have substantially plane-parallel surfaces free of dust and internal voids. 1 mm thickness Specimens were cut from the compression-molded sheet and the size of each test specimen was large enough to cover the entrance port of the sphere.

The PVC/MBS blends were tensile at a speed of 50mm/min at 23°C to a constant strain and the stress whitening phenomenon was recorded by a Canon scanner.

Transmission Electron Microscopy and Scanning Electron Microscopy

TEM samples were microtomed from PVC/MBS blends in order to examine the morphology of MBS. The specimens were cut to 60nm in thickness using a microtome at –100°C, and the samples were stained by exposing the ultrathin sections in the vapor of 1% OsO_4 solution over night before observation. A JEM-2000EX TEM operated at 200kv was used to study the deformation mechanisms.

Deformation mechanisms inside the stress-whitening zone of samples tested in Izod impact were observed by SEM (JSM-5600). The specimen was prepared by cryogenically splitting the impact-tested sample; the cryogenic fracture surface was perpendicular to the impact fracture surface and passed through the stress-whitening zone.

Results and discussion

Characteristic of MBS

Three MBS core-shell modifiers with different internal structures were synthesized in emulsion polymerization, and the different internal structure must lead to the different character of MBS. It is well known that normal MBS core-shell particle gives two tanδ peaks in the curve of DMTA: one, in the lower temperature, belongs to the rubber core phase; the other, in the region of about 100°C, belongs to the glassy shell phase. As shown in Figure 2, MBS1 had two Tg: one in the low temperature belongs to the homogenous SBR core and the other in the high temperature belongs to the shell. However, both MBS2 and MBS3 had three Tg: two Tg in the low temperature range belong to the hard core and soft inter layer shell, respectively; the Tg in the high temperature belongs to glassy shell. Table 2 gave Tg of the three MBS particles.

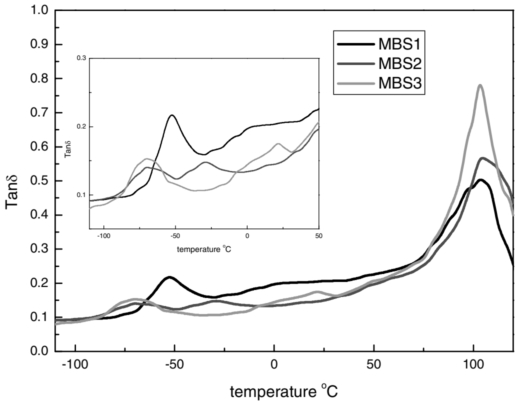
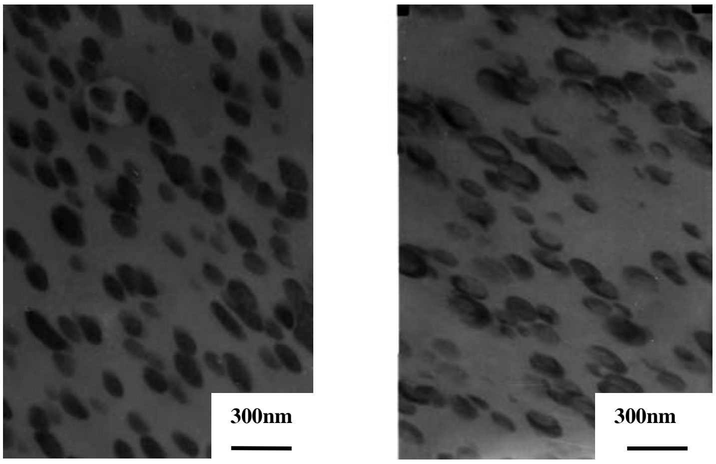


Figure 2 Tanδ as a function of temperature for MBS with different internal structure

Table 2 Tg of MBS core-shell modifiers employed in this study

	M/B/S	Structure	The Bd/St in the inter- core	Tg℃
MBS1	30/42/28	2L	75/25	-50, 103
MBS2	30/42/28	3L	50/50	-70, -29, 103
MBS3	30/42/28	3L	33/67	-71, 20, 103



(a) (b)

Figure 3 Morphology of PVC/MBS blends (a) MBS1 with two-layer structure (b) MBS3 with three-layer structure

TEM was used to character the internal structure of MBS core-shell particles. The TEM photographs of PVC/MBS blends were shown in Figure 3. It was clearly found that the MBS particles could disperse in the PVC matrix well. Since the OsO4 was used to stain the double bonds of butadiene, the MBS1 with a SBR core could be stained to dark as shown in Figure 3a. As shown in Figure 3b, in MBS3 the core with less butadiene showed a relative light gray and the inner layer with more butadiene showed dark. The TEM photograph confirmed the MBS core-shell particles with two-layer and three-layer structure further.

Mechanical properties of PVC/MBS blends

In Figure4 the Izod impact strength was plotted as a function of temperature for the different PVC/MBS blends. It was found that the addition of MBS into PVC matrix can improve the toughness of PVC effectively and the impact strength of blends increased with the temperature. At low temperature, all the brittle blends had a notched impact strength of 90-200J/m, independent of the type of MBS modifier used, and the fractured samples only showed light stress-whitening in a small volume of the material near the notch tip. At high temperature, all the ductile blends had notched impact strength about 1100 J/m. And the fractured samples showed intensive stress whitening in a large volume of the test sample. It can be also found that MBS with two-layer structure had the higher brittle-ductile transition temperature than that with three-layer structure. As to the three-layer structure particles, MBS3 with more St in the core and corresponding of more Bd in the inner layer had a lower brittle-ductile transition temperature than MBS2.

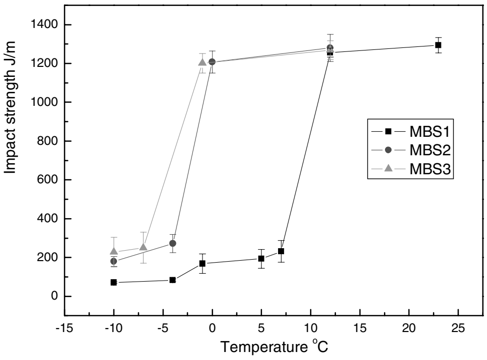
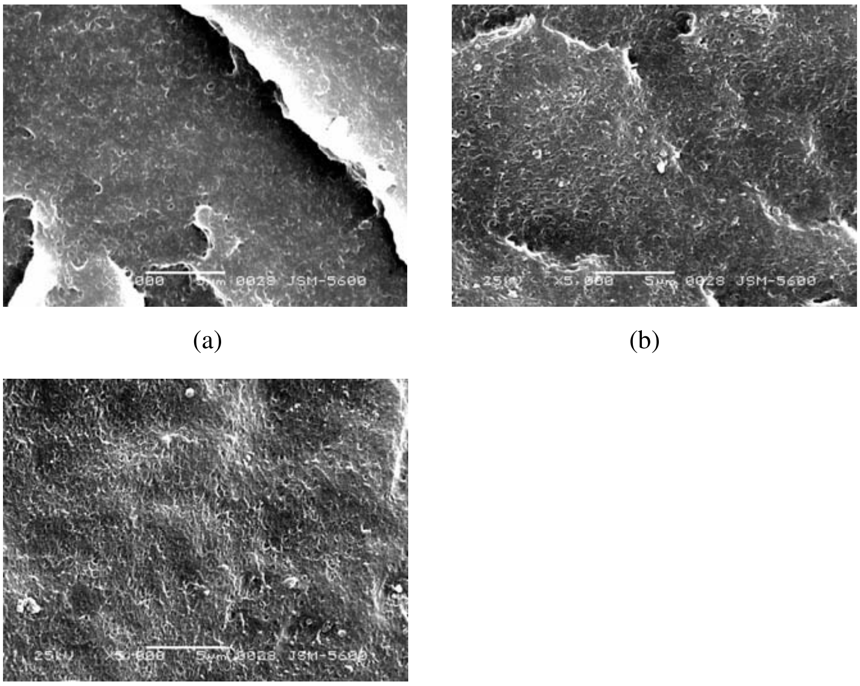


Figure 4 Izod impact strength as a function of temperature for different PVC/MBS blends

The influence of MBS particle morphology on the impact behavior of the blends could be related to the Tg of rubber of MBS modifier. Manson[17] have pointed out that in rubber toughened polymer, the rubber should have a Tg at least 60°C lower than test temperature to compensate for the high rate of deformation in an impact test. It suggested that the higher the Tg of rubber particles, the higher brittle-ductile transition temperature is. In MBS1 St copolymerized with Bd to form a single core with a higher Tg of -50°C ,which is the cause of the higher brittle-ductile transition temperature of PVC/MBS1 blend. As PS is a glassy polymer, the combination of styrene with butadiene must impair the elasticity of rubber, which is another cause of the MBS1 with a higher brittle-ductile transition temperature. Jiang [18] have quantitatively studied the effect of the elastomer stiffness on brittle-tough transition in elastomer toughening thermoplastic. They pointed out that the higher the modulus of the elastomer is, the higher the brittle-tough transition temperature of the blend is. The experimental results of Borggreve and Gaymans [19] also showed that the brittle-ductile transition temperature increases with modulus of the impact modifier in nylon-rubber blends. Van der Sanden [20] reported that the brittle-ductile transition temperature of PC/ethylene-propylene-diene monomer rubber (EPDM) blends increases with the modulus of EPDM rubber.

Freeze fracture technique is a useful method to study the deformation behavior of rubber-modified polymers [21]. Figure 5 showed the SEM observations on the cryofractured surface of stress-whitening zone of PVC/MBS blends. As shown in Figure 5(a) in the PVC/MBS1 blends with a two-layer structure, which had less stress whitening, only few cavities were observed and its size was close to the initial rubber particles. It was considered as the trails of rubber particles that were pulled out from the matrix. It can be seen from Figure5 (b) and (c) that when the MBS had the three-layer structure, there were massive cavities occur in the rubber particles, which could remove the plastic constraint and lead to a larger volume of plastically deformed material.



(a) (b)

(c)

Figure 5 SEM photographs of stress-whitening zone in PVC/MBS blends under impact test
(a) PVC/MBS1 (b) PVC/MBS2 (c) PVC/MBS3

The tensile properties of the different PVC/MBS blends were examined in a uniaxial tensile test at a strain rate of 50mm/min at room temperature, and the tensile data of the different PVC/MBS blends were shown in Table 3. It was found that the yield stress and elongation-at-break were the same within experimental error. Clearly, tensile mechanical properties were not influenced by the type of MBS used in this study. According to the Ishai–Cohen model [21], the tensile yield stress, $\sigma_{yt}(\Phi)$, of a composite containing a volume fraction, Φ, of low modulus inclusions can be expressed as follows:

$$\sigma_{yt}(\Phi) = \sigma_{yt}(0)\ (1\text{-}1.21\Phi^{2/3})$$

Where $\sigma_{yt}(0)$ is the yield stress of the matrix. It can be conformed that in our study the yield stress only depended on the effective rubber volume faction, and the morphology of the particle could not influence the yield stress greatly.

Table 3 Yield stress and elongation-at-break of PVC/MBS blends

Sample	Structure	Yield stress MPa	Elongation-at-break %
PVC/MBS1	2L	42.2	119.6
PVC/MBS2	3L	42.3	120.3
PVC/MBS3	3L	41.9	117.0

Transparency and Stress whitening of PVC/MBS blend

So far as rubber toughened transparent polymer is concerned, it must be remembered that two parameters are fixed by essential requirements of transparency:(a) the nature of the elastomer, whose refractive index must be equal to that of the PVC matrix; (b) the particle size, which must be small to avoid turbidity due to large sizes.

In general, it has been known that matching the refractive index of the rubber with that of matrix is difficult, because rubbers have relatively low refractive indices [22]. Therefore, the enhancement of the refractive index of the rubber has usually been can be achieved by combined with a monomer with appropriative refractive index. In MBS, St is acting as refractive index enhancer, which can vary the refractive index of MBS to match that of PVC. The refractive index of MBS can be calculated by the Gladstone-Dale relation as follow [23, 24]

$$\text{Refractive index (RI)} = \Sigma\, n_i v_i$$

Where n_i and v_i are the refractive index and the volume fraction of the components. According to this relation, all MBS designed to have the same chemical composition in our study will have the same refractive index. However, the transmittance of PVC/MBS blends with different internal structure was listed in table 4. It showed that MBS with the same chemical composition but different internal structure led to the difference in transparency, and the transmittance of blends with a 2L structure MBS had a higher value than that with a 3L structure MBS. As shown in Figure 3, when the MBS had a three-layer structure, there exist an inhomogeneous structure of glassy core and rubbery inner shell. There existed much phase interface in the MBS, which will lead to serious local optical inhomogeneity of the MBS and the decrease of transparency of the PVC/MBS blends. However, when the MBS had a two-layer

Table 4 Transmittance of PVC/MBS blends

Sample	Transmittance %
PVC/MBS1	85.7
PVC/MBS2	84.2
PVC/MBS3	82.7

structure, the optical inhomogeneity and the phase interface was decreased. These provided reason for the improvement of transparency of PVC/MBS blends with the changing of morphology of MBS from three-layer structure to two-layer structure.
Polymeric material under condition of mechanical deformation such as tensile, fatigue or impact loading have a tendency to exhibit a whiter appearance, in other words, an initially transparent or translucent polymeric material exhibits enhanced opacity and a whiter color leading to increased optical brightness, referred as “stress-whitening” [25,26]. In this study, the uniaxial deformation applied during stress-strain experiments generated stress whitening in initially transparent PVC/MBS blends. As shown in Figure 6, there existed an obvious different appearance in 2L particle and 3L particle. MBS1 with two-layer structure had slight stress whitening and MBS3 with three-layer structure had serious stress whitening.

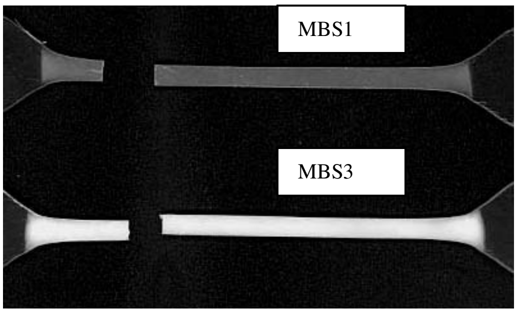


Figure 6 the stress whitening of tensile sample of PVC/MBS blends with different morphology of MBS

Conclusions

The influence of internal structure of core-shell modifier on the properties of PVC/ MBS blends was investigated. The results analysis illustrated that the internal structure of particles had significant effect on the glass transition temperature of MBS. The results of Izod impact tests showed that the MBS with a two-layer structure had a higher brittle-ductile transition temperature. Furthermore, the transparency of blend with two-layer structure MBS was higher than that with three-layer structure MBS. Microscope studies by SEM showed the cavitation of rubber particles and shear yielding were the main deformation mechanism of the blend with three-layer structure MBS.

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