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폴리염화비닐/PB-*g*-PMMA 복합재의 특징

Guangfeng Wu†, Hailong Zhang, and Huixuan Zhang

Engineering Research Center of Synthetic Resin and Special Fiber, Ministry of Education,
Changchun University of Technology

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Properties of Poly(vinyl chloride)/PB-*g*-PMMA Composites

Guangfeng Wu†, Hailong Zhang, and Huixuan Zhang

*Engineering Research Center of Synthetic Resin and Special Fiber, Ministry of Education,
Changchun University of Technology, Changchun 130012, P.R. China*

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Abstract: To improve the mechanical properties of poly(vinyl chloride) (PVC), the characters of combining PVC with elastomers were considered. Polybutadiene grafted poly(methyl methacrylate) (PB-*g*-PMMA, MB) core-shell particles were prepared by emulsion polymerization, and were used as an impact modifier for PVC. The impact resistance, fracture, brittle-ductile transition and the morphology of PVC/MB blends were investigated. It was found that MB particles had a high toughening efficiency for PVC resin, the impact strength was more than 1100 $J \cdot m^{-1}$ when MB was 8 phr. Two factors influence the impact strength and brittle-ductile transition, one is the modifier content, and the other is core-shell weight ratio. The impact curves are Ω-like shape, the impact strength value is the highest at the middle part and the PVC/MB blends show ductile break behaviors. The core shell ratio of ductile areas are limited from 80/20 to 90/10 for PVC/MB=100/8, and 70/30 to 93/7 for PVC/MB=100/10.

Keywords: polymer composite, toughened, brittle-ductile transition, core-shell particles.

Introduction

Toughness is often an important factor in thermoplastics selection. However, many plastics are brittle, particularly at low temperatures and during high speed impact. It is well known that the impact properties of these materials can be considerably enhanced by incorporation of a rubbery phase, often without the deterioration of other desirable properties. The main energy dissipative processes in rubber-toughened thermoplastics are massive matrix crazing, cavitations, and multiple localized shear bands initiated by the particles.[1] These phenomena are affected by the size, morphology, composition and volume fraction of the rubber particles, the adhesion between rubbers and matrix which are influenced by interphase thickness and the mechanisms of deformation of the matrix.

The role of the rubber particles is to modify the deformation behavior of the matrix polymer. The properties and composition of the matrix are therefore of paramount importance in determining the impact strength of a rubber toughened polymer. In general, the toughest rubber-modified plastics are those based on relatively ductile matrix polymer. Poly(vinyl chloride) (PVC) has been classified the pseudo-ductile polymer because it fails by shearing[2,3] and shows very high impact strengths. For this reason, the PVC/PB-*g*-PMMA(MB) blend can attain super-toughness (notched Izod impact strength > ca. 500 $J \cdot m^{-1}$).

It has been proposed that the PVC matrix require certain special rubber phase morphology for super-toughness. This special morphology is the pseudo-network morphology.[3] Z. H. Liu[4-7] and other researchers[8,9] have been observed three morphologies: pseudo-network morphology, network morphology, and morphology of well-dispersed particle.

A comprehensive description of synthesis of core-shell structured MB particles and its dispersion in PVC matrix was given in the previous article.[10] We found that the PVC/MB

†To whom correspondence should be addressed.
E-mail: gfwu20@163.com

blends with the best mechanical properties could be obtained when the core-shell ratio of polybutadiene (PB) to poly(methyl methacrylate) (PMMA) is lower than 93/7. This mechanical change point can be called the first brittle-ductile transition point. During the following study we found another brittle-ductile transition point existing at core-shell ratio (B/M) is around 80/20 (wt%). This article focuses on the second brittle-ductile transition and the corresponding morphology change in PVC/MB blends.

Experimental

Materials. The polymers used in this work were commercial grade of poly(vinyl chloride) (PVC SG-5, K=66), PB latex (solid content 59%) and methyl methacrylate (MMA), they were provided by Jilin Chemical Co. LTD., China.

Sample Preparation. Poly (methyl methacrylate) (PMMA) was grafted on polybutadiene (PB) latex particles to prepare PB-*g*-PMMA (MB) core-shell particles by emulsion polymerization as same as in the article,[10] the recipes are shown in Table 1.

PVC/MB blends of varying MB content were milled on two roller mill (made by TianJian Mechanical Plant) at 160 ℃ for 5 min. These milled sheets were stacked together and compressed-molded at 185 ℃ and 15 MPa pressure for 5 min, and then cooled slowly down to the room temperature. The samples for impact tests and morphological observations were cut from these plates.

Measurement of Latex Particle Diameter. The MB particle diameter and their distribution were measured by BROOKHAVEN 90-Plus laser particle analyzer (Brookhaven Instruments Corporation).

Impact Tests. The notched Izod impact strength of PVC/MB blends were measured by Izod AJU-22 impact tester according to ASTM-D256 standards.

SEM Observation. The samples were cro-fractured. The fracture surfaces were etched in toluene at 20 ℃ for 5 h to remove MB phase. Then, they were coated with Au. The morphologies were observed in a JEM-5500EX scanning electron microscope (SEM).

Table 1. Formulas of MB Emulsion Polymerization

Polymers	Core PBL (kg)	Shell MMA monomer (kg)	Core-shell weight ratio (B/M)
PB	14	0	100/0
MB1	14	0.894	94/6
MB2	14	1.054	93/7
MB3	14	1.217	92/8
MB4	14	1.556	90/10
MB5	14	2.470	85/15
MB6	14	3.500	80/20
MB7	14	6.000	70/30
MB8	14	9.330	60/40
MB9	14	14.000	50/50

Note: Deionized water 20 kg; Potassium oleate/M (1%); Redox initiator/M (0.7%).

Results and Discussion

Synthesis of Core-shell Latexes. The PB/PMMA core-shell latex was synthesized according to the procedures described previously.[10] As we known, when we incorporate MB core-shell particles with PVC resins to get PVC/MB blends, the core-shell particles are interphase. The interphase thickness, which is the PMMA shell thickness influence the adhesion of the PB rubber particles to the PVC matrix. We must increase the shell thickness as large as possible to keep the properties in a better level. As a basic, we synthesized a series of MB particles which have PMMA-shell thickness gradient, the corresponding core to shell ratio is change from 94/6 to 50/50 (wt%). The PMMA-shell thickness values are listed in Table 2.

In the blends of rubber toughened plastics, the rubber acts as the main roles of absorbing the fracture energies. The rubber balls with different diameter have an obvious difference in absorb energy, so only when the diameter of all of rubber balls

Table 2. Principle Characteristics of the MB Latex Particles

Polymers	Core-shell weight ratio (B/M)	Particles size (nm)	PMMA-shell thickness (nm)
PB	100/0	318	-
MB1	94/6	325	3.9
MB2	93/7	328	4.6
MB3	92/8	331	5.3
MB4	90/10	338	7.7
MB5	85/15	351	9.2
MB6	80/20	365	11.7
MB7	70/30	380	15.2
MB8	60/40	395	18.7
MB9	50/50	406	18.2

equaled, can we compared the toughened efficiency of modifiers. In the experiment, a batch of PB emulsion were divided into several parts, each part is act as the seeds of the modifier rubber core, this methods can guaranteed the rubber core has the same diameter. Then we changed the MMA amounts to adjust the thickness of PMMA plastics shell.

Mechanical Properties of PVC/MB Blends. PB rubber is incompatible with PVC resins,[5] so it is necessary to graft PMMA onto the surface of ball-like PB particles, forming the miscible shells to blend with PVC.[6] We grafted PMMA onto PB particles according to core-shell weight ratio from 50/50 to 94/6. Figure 1 shows the relation between the notched Izod impact strength of the blends and the MB core-shell weight ratio. As can be seen from Figure 1, when MB contents is 8 phr (percent of a hundred resin, phr), the notched Izod impact strength of the PVC/MB blends are lower than MB is 10 phr's, that is, the higher of MB content, the higher toughening effectiveness of MB modifiers. The impact curves are Ω-like shape, the impact strength value is the highest at the middle part and the PVC/MB blends samples show ductile break behaviors. The core shell ratio of ductile areas are limited from 80/20 to 90/10 for PVC/MB=100/8, 70/30 to 93/7 for PVC/MB=100/10, respectively.

The Ω-like curves indicate that the PVC/MB blends have two brittle-ductile transition areas (BDTA): area II and IV, as shown in model curve of Figure 2. In BDTA, the notched Izod impact strength of the blends is changed obviously with the core shell ratio of MB. In area I and V, the impact break is in a typical brittle fashion, and the impact strength values are very low. In the ductile area III, the impact strength values of PVC/MB blends are the highest, this recipe is valuable.

With we change MB content in PVC/MB, different BDTA points are variable. When MB content is 8 phr in PVC/MB blends, the BDTA points extend as far as to 80/20 for area II, and from 90/10 to 92/8 for area IV. But for MB content is 10 phr in PVC/MB blends, the BDTA points are changed from 50/50 to 70/30 for area II, and from 93/7 to 94/6 for area IV. This can be seen clearly in Figure 1.

The experiments found that the BDTA becomes thinner when MB content increase in the PVC/MB blends.

Figure 3 shows that the tensile strength values of the PVC/MB blends decrease with the MB content increase from 8 to

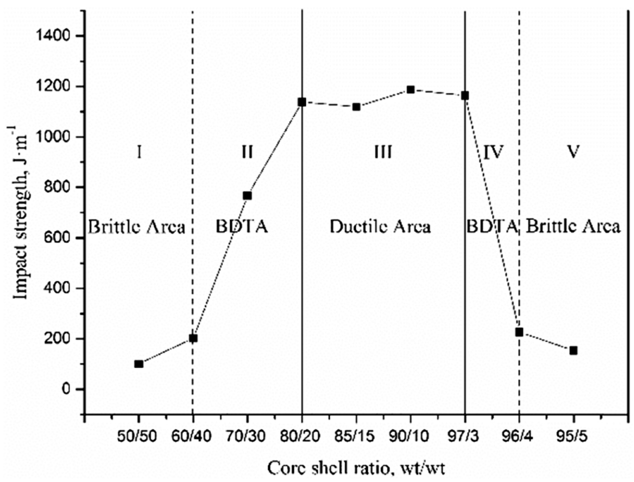

Figure 2. Model of areas in notched impact strength of PVC/MB blends.

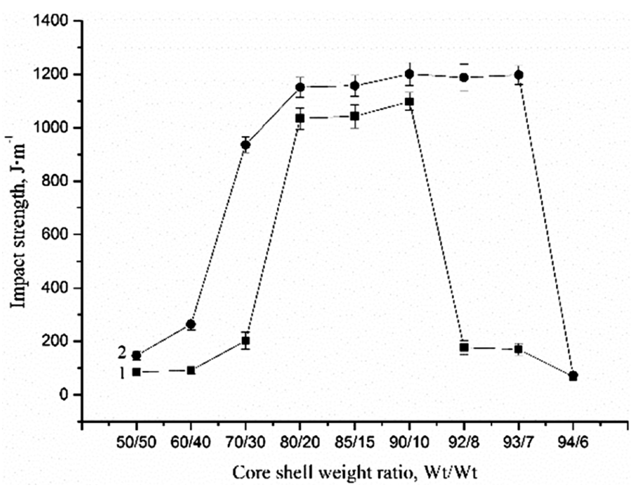

Figure 1. Influence of MB core shell weight ratio on notched impact strength of PVC/MB blends. (1) PVC/MB=100/8; (2) PVC/MB=100/10.

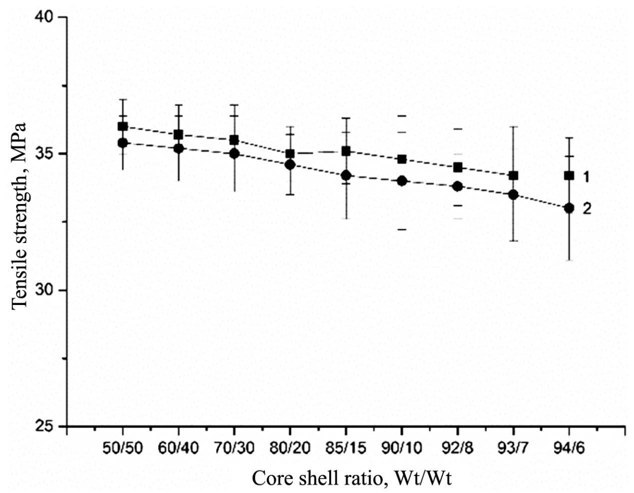

Figure 3. Influence of MB core-shell weight ratio on tensile strength of the PVC/MB blends. (1) PVC/MB=100/8; (2) PVC/MB=100/10.

10 phr, and also decrease slightly with the core shell ratio of MB change from 50/50 to 94/6.

Morphology of Fracture Surface. PVC/MB blends are failure in manner of brittle fracture and ductile fracture.

Figure 4 shows SEM photographs of the impact fracture surface of the PVC/MB (100/8, wt/wt) specimens. Figure 4(a) is the fractured surface photo of PVC blend with MB7 (core-shell weight ratio 70/30), the relatively smooth fracture surface show little matrix yielding, characteristic of brittle failure (below 200 J·m^{-1}). Figure 4(b), the fracture surface of blend with MB5 (core-shell weight ratio 85/15), is rough and has large number of fibrils and voids, show extensive matrix yielding, which suggests that the impact specimen breaks by yielding. It is a typical facture surface of a ductile fashion.

The results prove that it has two factors influence the impact strength in rubber toughened plastics blends.[1,11-15] One is the rubber content, the other is core-shell ratio. MB7 core-shell weight ratio lower than 70/30, MB5 lower than 80/20, the blends break in a brittle fashion, because the rubber content is not enough to toughen the PVC resin. When the core-shell weight ratio is higher than 93/7 in 100/10 blends and 90/10 in 100/8 blends, the brittle fracture is occurred because the PB core cannot be totally covered with PMMA, resulting in the rubber particles coagulations in the PVC matrix. But it still exists strong adhesion between MB and PVC matrix, it means that MB particles can still absorb a certain amount of impact energies. The absorbed energies have different contribution in different blends. In 100/8 blends, the impact energies absorbed by MB particles are not enough to overcome the defects caused by coagulation so that the materials show brittle fracture behaviors when the core-shell weight ratio is higher than 90/10. However the materials have more rubber content in 100/10 blends, the ability of MB particles toughening matrix plays a decisive position than coagulation. Therefore, the blends still have better mechanical property than 100/8 blends when the core-shell weight ratio higher than 90/10.

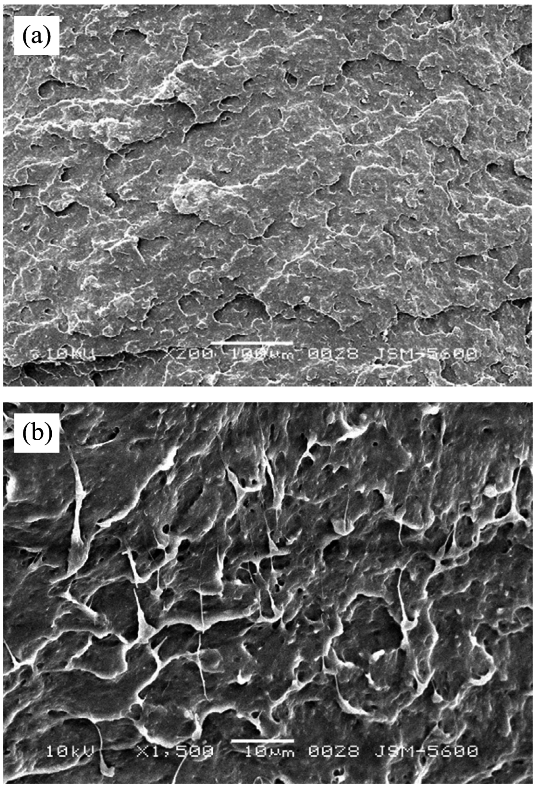

Figure 4. SEM photographs of the impact fracture surface of the PVC/MB blends.

Wu[10] has studied the effect of rubber-matrix adhesion. Strong adhesion alone is not sufficient for toughening, but the minimum adhesion required for toughening is proposed to be about 1000 J·m^{-1}. Obviously, the miscibility of PMMA with PVC can ensure good adhesion between rubber particles and matrix, while the PMMA shells can hardly be regarded as a part of the rubbery phase. To take this fact into account, we have converted the weight fractions into volume fractions and subtracted the fractions of PMMA grafts.

Distribution of MB in PVC Matrix. PVC resin has three particulate structures, domain, primary particles and resin grain.[10] The particulate nature of PVC is responsible for the morphologies of PVC/rubber blends. Liu[6] has been observed three different morphologies of PVC/rubber blends: the pseudo-network morphology, the network morphology, and the morphology of well-dispersed. The rubber particles in the blends with the pseudo-network morphology act as stress concentrators to promote matrix shear yielding or crazing, and absorb a very small amount of impact energy. The role of the rubber particles in these PVC/rubber blends is the same as that of rubber particles in the blends with the morphology of well-dispersed. However, the continuous rubber phase in the blends with the network morphology directly absorbs a large amount of impact energy. So, the toughening mechanisms for the two morphologies are different.

In this work, we study the effect of MB particle distribution on the impact toughness of PVC/MB blends. Figure 5 shows that the MB particles are dispersed in the PVC matrix. Figure 5(a) shows the well-dispersed morphology in the PVC/MB (PVC/MB, 100/10, wt/wt) blend with the MB core-shell weight ratio is 60/40. Figure 5(b) shows the pseudo-network morphology, the MB core-shell weight ratio is 85/15. The

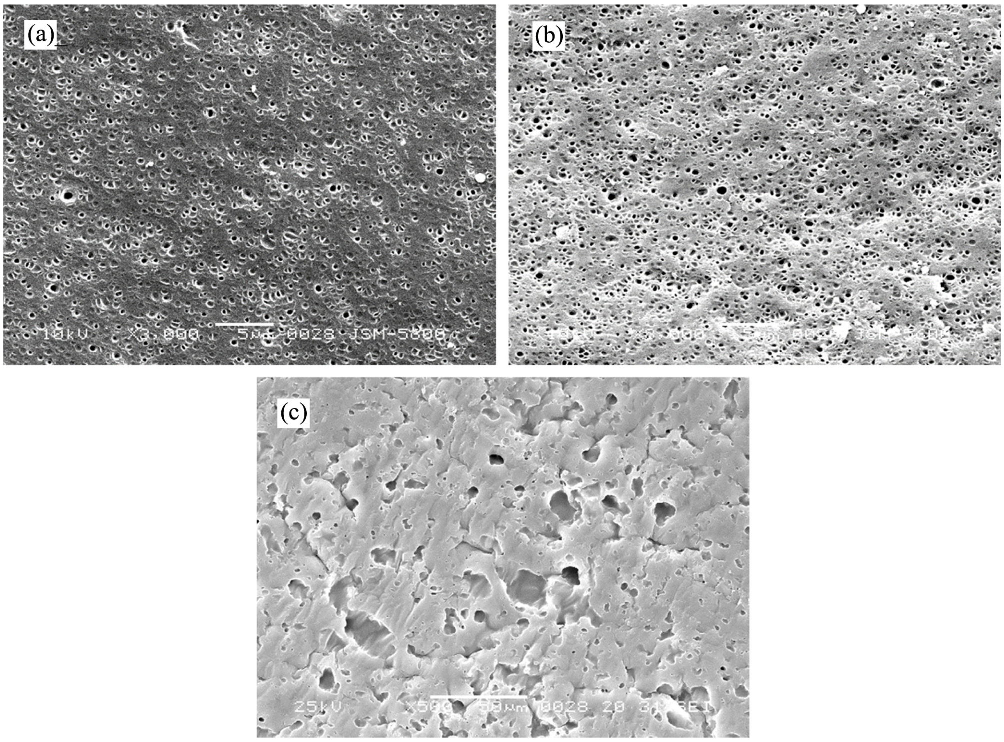

Figure 5. Disperse of MB particles in the PVC matrix.

notched Izod impact strength of this sample is 1100 J·m^{-1} and the fracture surface is full of stress-whitened area. It indicates that the mechanism of this sample fracture is yielding. In Figure 5(c), it has a serious coalescence in the blend with MB core-shell weight ratio 94/6, which is further proved why the sample shows a brittle fracture.

Conclusions

MB particles have a high toughening efficiency for PVC resin. In this work, two types of morphologies have been found: the morphology of well-dispersed particles and the coalescing morphology. Brittle-ductile transitions have been observed in PVC/MB blends by plotting impact strength against MB weight fraction and the core-shell ratio. The Ω-like curves of PVC/MB blends have two brittle-ductile transition areas (BDTA), are named as area II and IV, we can prepare a super toughened PVC/MB alloys in area II. That is to control the core shell ratio from 80/20 to 90/10 for MB content is 8 phr in PVC/MB blends, or control the core shell ratio from 70/30 to 93/7 for MB content is 10 phr in PVC/MB blends.

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References

1. P. Norbert, *J. Polym. Sci.: Polym. Lett. Ed.*, **18**, 643 (1980).
2. S. H. Wu, *Polymer*, **26**, 1855 (1985).
3. S. H. Wu, *Polym. Eng. Sci.*, **30**, 753 (1990).
4. Z. H. Liu, X. G. Zhu, L. X Wu, Y. Li, Z. N Qi, C. Choy, and F. Wang, *Polymer*, **42**, 737 (2001).
5. Z. H. Liu, X. D. Zhang, X. G. Zhu, R. K. Y. Li, Z. N. Qi, F. S. Wang, and C. L. Choy, *Polymer*, **39**, 5019 (1998).
6. Z. H. Liu, X. D. Zhang, X. G. Zhu, Z. N. Qi, F. S. Wang, R. K. Y. Li, and C. L. Choy, *Polymer*, **39**, 5027 (1998).
7. Z. H. Liu, X. G. Zhu, Q. Li, Z. N. Qi, and F. S. Wang, *Polymer*, **39**, 1863 (1998).
8. M. C. Michael, C. P. Paul, and F. G. John, *Specific Interactions and the Miscibility of Polymer Blends*, Technomic Publishing Co., Pennsylvania, 1995.
9. J. Kolarik, L. D. Landro, and M. Pegoraro, *J. Mater. Sci. Lett.*, **9**, 876 (1990).
10. G. F. Wu, J. F Zhao, H. T. Shi, and H. X. Zhang, *Eur. Polym. J.*, **40**, 2451 (2004).
11. G. P. William, *Polym. Eng. Sci.*, **39**, 2445 (1999).
12. D. S. Parker, H.-J. Sue, J. Huang, and A. F. Yee, *Polymer*, **31**, 2267 (1990).
13. A. Yanagase, M. Ito, N. Yamamoto, and M. Ishikawa, *J. Appl. Polym. Sci.*, **60**, 87 (1996).
14. J. C. Lim and K. E. Min, *Polym. Korea*, **20**, 558 (1996).
15. Z. H. Liu, X. D. Zhang, X. G. Zhu, R. K. Y. Li, Z. N. Qi, F. S. Wang, and C. L. Choy, *Polymer*, **39**, 5035 (1998).