Journal of Applied Polymer Science

Phase Morphology and Dynamic Mechanical Behavior for MIS Toughened Polyvinyl Chloride

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ABSTRACT: Graft copolymers of isoprene (Is), styrene (St), and methyl methacrylate (MMA) monomers (MIS) with typical core–shell structure were synthesized by seed emulsion polymerization and used as a toughening agent for preparation of polyvinyl chloride (PVC)/MIS blends. The St and MMA monomers were separately grafted on the cross-linked poly-isoprene rubber core. The toughness, sub-micro-morphology, and dynamic mechanical behavior of the blends were characterized by impact machine, scanning electron microscopy (SEM), and dynamic mechanical analyzer. The results showed that the impact strength of the blends was optimized when the content of MIS in PVC/MIS blends was kept at a constant value of 8 wt %, while the content of Is in MIS was 70 wt %. SEM morphologies of impact fractured surface showed that the PVC/MIS blends were typical ductile fracture because of the toughness effect of rubber particles, which correlated well with the mechanical properties. Under the same rubber content condition, the curves of the dynamic mechanical behavior of MIS toughened PVC blends appeared a more obvious rubber peak, indicating that the rubber content of MIS was higher than that of methyl methacrylate–butadiene–styrene (MBS), which explained the better toughening effect of MIS compared with MBS. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 3466–3472, 2013

KEYWORDS: resins; synthesis and processing; rubber; plasticizer; morphology

Received 9 November 2012; accepted 25 January 2013; published online 28 February 2013
DOI: 10.1002/app.39095

INTRODUCTION

Polyvinyl chloride (PVC) is a widely used general-purpose plastic due to its excellent overall performance. It has been extensively used in construction, transportation, and many other industries thanks to its versatility, being relatively cheap, high stiffness, and good chemical resistance. However, PVC application has been restricted[1–3] because of its disadvantages, such as brittle fracture, bad toughness, and low heat resistance. Thus, improvement of toughness is highly concerned to enhance its application performance.[4]

Therefore, extensive research and development works have therefore been carried out to formulate polymers with high impact resistance. As is well known now, the impact properties of plastics could be considerably strengthened by addition of a rubbery phase. One successful method of rubber[5] toughening involves the addition of elastomeric particles into a polymer matrix. The rubber particles are dispersed in the plastics matrix and act as stress concentrators to promote crazing or shear yielding of the matrix, which forms the dominant toughening mechanism to improve impact strength.[6]

Being compatible with the matrix, core–shell[7] modifiers are widely used in PVC,[8] whereafter they have gradually been applied in other polymers such as polycarbonate (PC),[9,10] polybutylene terephthalate (PBT),[11,12] PBT/PC,[13] and polymethylmethacrylate (PMMA).[14–16] As a universal toughening modifier, methacrylate–butadiene–styrene (MBS) polymer with a rubber core of PB and outer shell of PMMA was originally synthesized through emulsion polymerization[17] in 1958,[18,19] wherein PB endows materials with impact resistance, while the grafted PMMA-shell plays a primary role of improving the compatibility and rigidity of the PVC matrix. Many factors can influence the impact strength and brittle ductile transition in rubber toughened plastics blends, such as the modifier content, cross-linking density, and the core–shell ratio.

Arakawa et al.[20] have studied the effect of rubber particle size with a bimodal particle size distribution on the impact tensile fracture behavior of MBS resins. The results of Takaki et al.[21] also suggested that the cross-linking degree of MBS determined the impact strength of PVC/MBS blends. The impact strength of the blends was improved with the decreased cross-linking degree of rubber.

With the progress of petroleum industry, isoprene (Is) has become more economical and easier to control in the process of polymerization compared with butadiene.[22–26] In this work, butadiene was replaced by Is during the process of toughening modifiers synthesis. Ternary copolymer MIS with typical core–shell structure was successfully synthesized and used for toughening PVC. Scanning electron microscopy (SEM) and dynamic mechanical analyzer (DMA) were used to study the influence factors of blends toughness. At the same time, further study was done on two systems to study the factors that affect impact toughness of the blends. Several PVC specimens with different MIS contents and another PVC blends with the same MIS content but different Is contents were also selected to explore the key factors determining the impact toughness of the PVC/MIS blends.

EXPERIMENTAL

Materials

Is, styrene (St), butyl acrylate (BA), and methyl methacrylate (MMA; supplied by Qilu Corporation of Sinopec, Zibo, China) were used as monomers. Sodium dodecyl sulfate and potassium persulfate were, respectively, employed as emulsifiers and initiators (supplied by Zibo Dong Da Chemical Stock Co., Zibo, China). Double-distilled and de-ionized water was used throughout the polymerization. In order to compare with the self-made MIS, MBS (BTA-751), and (B-625; supplied by Daikin Dong guan Plastic Materials Company, Dong guan, China) were adopted as processing aids. PVC resins were supplied by Jilin Chemical Company, Jilin, China.

Synthesis of MIS

Synthesis of Latex with Large Size Particles by Seed Emulsion Polymerization. The latex with large size particles could be prepared mainly by two-stage emulsion polymerization. The reaction was performed in a 1 L high pressure reactor under a nitrogen atmosphere at 65°C with the stirring speed of 300 rpm. First, the de-ionized water, Is, initiators, and emulsifiers were added into the reactor and stirred for 6 min under nitrogen, and then the St monomers mixed with initiators were charged. The reaction was stopped with monomer conversion of 95%, and we got the latex with small size particles, which were used as the "seed" for subsequent process. A series of latex with large size particles could be synthesized separately by adding Is monomer into 5, 10, 15, and 20 g of seed latex and allowing the latex size enlarging reaction to proceed under similar conditions of seed polymerization, during which the newly added Is continued to grow on the "seed" and the latex size could be controlled by different dosages of seed latex.

Grafting Emulsion Polymerization. The graft polymerization of the monomer proceeded according to the mechanism of emulsion polymerization.[26] The latex with large size particles, the de-ionized water, St, MMA, emulsifiers, and initiators were successively added into the reactor and stirred at 65°C. The graft polymerization of MMA and St continued for 3 h, and the first grafting latex was obtained. The second grafting reaction started after MMA, BA, emulsifiers, and initiators were added, respectively. After that, St and MMA monomers were separately grafted to poly-isoprene (PI) latex particles and formed MIS core–shell structure.

Coagulation of Grafting Latex. De-ionized water and $CaCl_2$ coagulant were stirred and heated in a glass beaker in advance, and then a mixture of antioxidant and grafting latex was added slowly into the beaker when it reached 35°C. The graft latex obtained from emulsion polymerization was coagulated and formed loose aggregates. MIS resin particles could be obtained by heating up to 80°C and held for 20 min. Finally, we got the pure MIS resins after a series of centrifuging, filtering, washing, and drying at 50°C.

Determination of MIS Grafting Ratio. MIS particles (0.05 g) were completely extracted by acetone in reflux condition for 24 h in a Soxhlet extraction apparatus and centrifugalized for 30 min to collect supernatant fluid, and then repeat the above procedures with appropriate amount of acetone. Dissociative PMMA and PS, which were not grafted onto PI rubber, were fully removed from the PI particles surface. Thus, the remaining deposit was totally grafted MIS. By drying and weighting the deposit, the grafting ratio of MIS was calculated and defined as the percentage of grafted shell versus the total content of PI core.

Preparation of PVC/MIS (MBS) Blends

Blends of PVC/MIS (MBS) were prepared by mixing and melting PVC, MIS (MBS), heat stabilizer, and lubricant on two-roll mill (made by Dong guan Xi hua Testing Machine Co., Dong guan, China) for 6 min with blending temperature of 170°C and roll speeds of 10 m/min and 12 m/min. The specimens used for impact test were prepared by a compression-molding machine (made by Dong guan Xi hua Testing Machine Co.) operating at 185°C and 15 MPa pressure for 8 min. The specimens were set to 4 mm thickness with a notch length of 0.20 mm and conditioned overnight at 25°C before the Izod impact tests.

Measurements

Impact Testing. The impact properties of composite samples were measured by universal testing machine (Type XJJ-5, ChengDe Precision Co., ChengDe, China) according to ISO 180:2000. The impact tests were carried out in a conditioned room with a constant humidity of 45% and temperature ranging from 23 to 25°C.

Scanning Electron Microscopy. The phase morphologies and fractured surfaces of notched impact specimens were observed by SEM (HITACHI H-7000, with scanning accessory) with operating voltage of 15 kV and a magnification of 10,000, in order to analyze and compare the impact-modified and -unmodified samples. The fractured surfaces were sputter-coated with a thin gold layer before observation.

Dynamic Mechanical Analysis. The DMA measurements were carried out on a Q800 Dynamic Mechanical Analyzer (TA Instruments Co., New Castle) in single cantilever mode. Specimens were measured at a frequency of 2.0 Hz and a heating rate of 5°C/min with the temperature ranging from −90°C to 140°C under nitrogen flow. The specimens were prepared with dimensions of 10 mm width, 2 mm thickness, and 35 mm length, and measurements of all the samples were made at identical conditions.

RESULTS AND DISCUSSION

Seed Emulsion Polymerization and Determination of MIS Grafting Ratio

Seed emulsion polymerization was adopted to prepare the grafting copolymer MIS with core–shell structure. The polymerization took place on the particles of seed latex. When grafting monomers were added into seed latex, MMA monomers diffused onto emulsion particles and polymerized, wherein a part of MMA was grafted on the un-reacted double bonds of PI latex particles and covered on the surface of them, and the other part of MMA monomers covered on the surface of PI particles through interpenetrating polymer networks after polymerization. These two parts of PMMA formed the shell of grafted copolymer with core–shell structure. The feeding rate of monomers, as well as the contents of emulsifier and seed latex, will influence MIS grafting ratio.

MIS grafting ratio was determined with Soxhlet extraction apparatus, and the results are shown in Figure 1. It can be seen from Figure 1 that MIS grafting ratio, one of the important parameters influencing impact resistance, decreased with the increase of the Is content in MIS. When grafting ratio is too high, the proportion of rubber particles is decreased, weakening the capability of initiating vacancy and crazes, resulting in bad impact resistance, while grafting ratio is too low, the grafted amounts of MMA and St on PI particles are not enough to cover all the rubber particles, leading to poor compatibility of MIS with PVC matrix and thus bad impact resistance; therefore, the optimal MIS grafting ratio should be 15–25%.

Impact Performance Comparison between PVC/MIS and PVC/MBS Blends

Effect of Is Content in MIS on the Blends' Impact Resistance. It is well known that the impact resistance of PVC blends plays an important role in final application, and the core–shell ratio can significantly influence the impact strength in rubber toughened PVC blends. Therefore, MIS resins (8 wt % based on the blends) with different Is contents were added into PVC matrix. Figure 2 illustrates the relationship between impact strength and Is content of PVC/MIS blends.

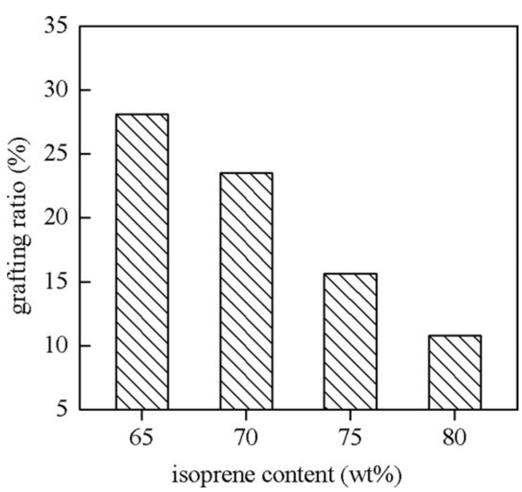

Figure 1. The effect of Is content in MIS on the grafting ratio.

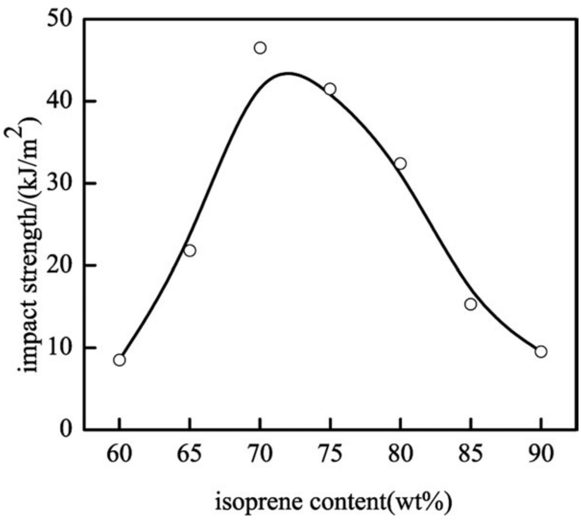

Figure 2. The effect of Is content in MIS on the impact resistance of the blends.

It was found that the impact strength of the blends increased with the increasing Is content. It reached the highest value of 42 kJ/m^2 at the Is content of 70 wt %, and then it decreased gradually. This phenomenon can be explained by the core–shell structure of MIS and its properties. As the stress concentrator points, the rubber core induced craze and shear, which absorbed more energy and produced ideal modifying effect with increasing content of Is. But the perfect core–shell structure would not be formed if the Is content reached more than 80 wt %, which may lead to poor compatibility of MIS with PVC, affecting the toughening effect and leading to decline in impact strength. Generally, it was of high toughening efficiency with the Is content range from 70 wt % to 80 wt %.

Influence of MIS Percentage in Blends on Impact Strength. As another influence factor on the impact strength and brittle ductile transition, the modifier content has been investigated as illustrated in Figure 3, wherein different percentages of MIS resins at the same Is content of 70 wt % were added into PVC.

Figure 3 also shows that the impact strength increased with the increasing MIS content at first. It experienced a rising peak and then gradually declined, indicating that the maximum impact strength appeared at 8 wt % content. However, the samples broken brittlely, and brittle–ductile transition did not exist at all, which meant modifiers had not toughened PVC, when the content was less than 3 wt % or more than 15 wt %. With the increase of stress intensity points, the rubber core produced more craze and shear and thus absorbed more energy, which had brought good modifying effect.

Effect of Toughening Type on Impact Strength. Conventional MBS and the MIS resins, whose rubber content was kept at 70 wt %, were, respectively, mixed with PVC at the same content of 8 wt %, and the modifying effect for PVC resins was compared. In Figure 4, the notched Izod impact strength data of MBS (B-625) and MBS (BTA-751) toughened PVC were, respectively, shown as 8.6 and 15.2 kJ/m^2. However, the Izod impact

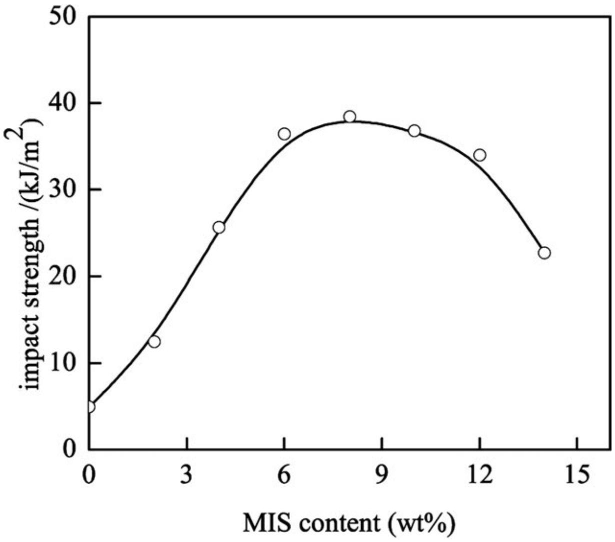

Figure 3. The effect of the percentage of MIS on impact strength.

strength increased dramatically with the increase of MIS amounts. As shown in Figure 4, the notched impact strength was nearly five times as high as that of MBS toughened PVC with 9 g modifier in 100 g PVC resins. A large stress-whitened area was formed near the fractured surface. Obviously, the impact strength of PVC/MIS was superior to PVC/MBS.

Morphological Analysis of the Blends

Impact Fractured Surfaces of the Blends with Various Tougheners. The impact fractured surfaces of PVC, PVC/MBS (BTA-751), and PVC/MIS blends were compared to clarify the toughening mechanism of MIS. The content of MIS and MBS resins in the blends were, respectively, kept at a constant value of 8 wt %. Figure 5 displays the SEM micrographs of impact fractured surfaces of different blends at low temperature.

As shown in Figure 5(a), the impact fractured craze seemed little, neat, and orderly arrayed before the toughening agent was added, indicating a characteristic of typical brittle fracture. However, from the microstructure SEM picture Figure 5(d), we cannot find pronounced yielding or deformation in the PVC/MBS blends. It is well known that energy absorption mechanism of rubber particles consists of not only tearing and rubber cavitations, but also crazing and deformation of matrix.[5,7] Many root-like whiskers, vacancy, and more evident crazes were observed in PVC/MIS in Figure 5(e,f) micrographs, which could improve the impact performance dramatically. The micrographs can also clearly show the ductile yielding and fibrillation associated with crack termination in a hinge-break sample under different magnifications. Thus, the material realized the transition from brittleness to toughness. In comparison with MBS, MIS system got more obvious roots, cavitations structure, and better toughness.

Impact Fractured Surface of the Blends with Various Is Contents. Used as toughener, MIS with different Is contents were prepared and mixed with PVC. Since the rubber phase played a key role in the impact performance of the blends. The impact tests of the blends were conducted, and the fractured surfaces morphology of impact specimens were observed. Figure 6 shows the SEM micrographs of fractured surface for the blends.

Many layered structure and "fibrous" could be seen from Figure 6 when Is content was 65 wt %, which showed ductile fracture characteristics but insufficient vacancy. While the impact fracture seemed relatively smooth and lots of roots and obvious cavitations phenomenon appeared in Figure 6(b), suggesting obvious sea-island structure. Many long stretches of the ligaments are striking, and a large stress-whitened area was formed near the fractured surface, which suggests that the impact specimen breaks yieldingly. Compared with Figure 6(b), irregular whisker and fewer cavitations are displayed in Figure 6(c). Figure 6(d) shows uneven layered structure appearing on the fracture at 80 wt % Is content, which was nearly similar to Figure 6(a). Being coincident with the impact results, the vacancy of the plastic substrate could absorb more impact energy and improve the impact strength of the blends effectively.

Dynamic Mechanical Behavior of blends

DMA was used to study the influence of the internal structure of core–shell particles on the properties of pure PVC, PVC/MBS (BTA-751) blends, and PVC/MIS blends. The content of MIS and MBS resins in the blends were also kept at 8 wt %. The tan δ curves, which were often expressed as mechanical damping or internal friction, were measured at a frequency of 2.0 Hz with the temperature ranging from -90°C to 140°C as illustrated in Figure 7.

It showed that the glass transition temperatures of the PVC/MBS and PVC/MIS blends were higher than that of PVC. Compared with the PVC matrix, an additional interfacial phase existed in the blends, that made T_g of the blends increase accordingly. PVC/MBS blends had a relatively higher absorption peak at 70°C, indicating the absorption of MMA, than PVC/MIS. As the shell of the rubber particles, MMA had nice rigidity and compatibility with PVC, and that made MBS possess better

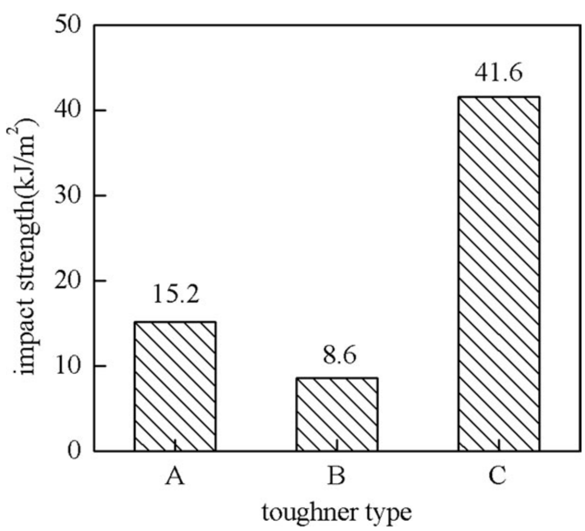

Figure 4. The effect of various tougheners on impact strength.

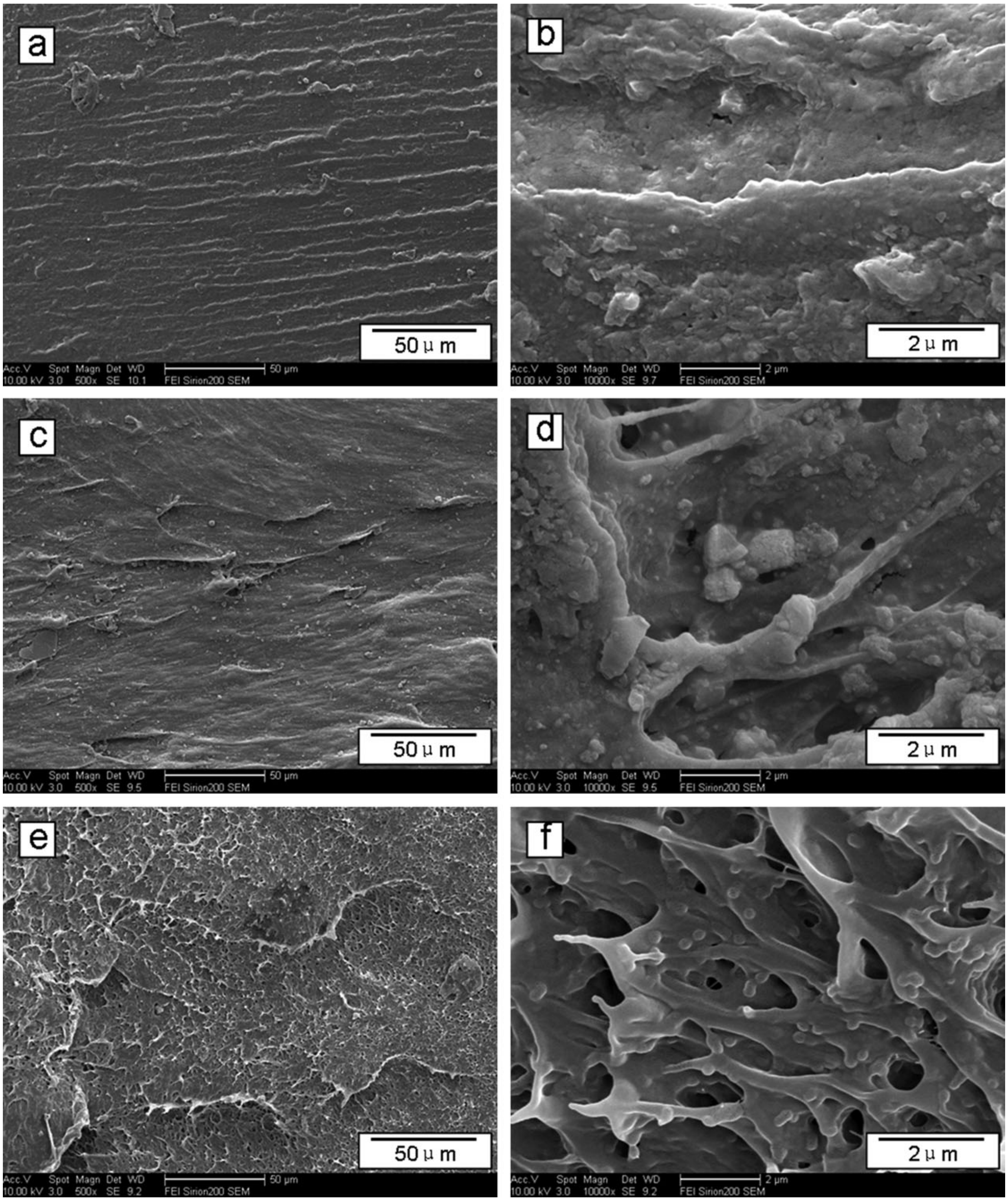

Figure 5. SEM images of the blends at different magnification rates: (a,b) PVC, (c,d) PVC/MBS, and (e,f) PVC/MIS.

rigidity than MIS. From the magnified picture, a more obvious rubber peak at −25°C could be seen in PVC/MIS blends. It is known to us all that the rubber phase played a role of toughener. Therefore, MIS had more remarkable toughening function compared with MBS, which was also consistent with the above test results of impact strength and morphology.

CONCLUSIONS

As a new PVC impact modifier, MIS resins, which could significantly improve the toughness of PVC, were synthesized. The optimal MIS grafting ratio ranged from 15% to 25%. The results of impact tests illustrated that the deformation of PVC/MIS blends could absorb massive impact energy. The impact

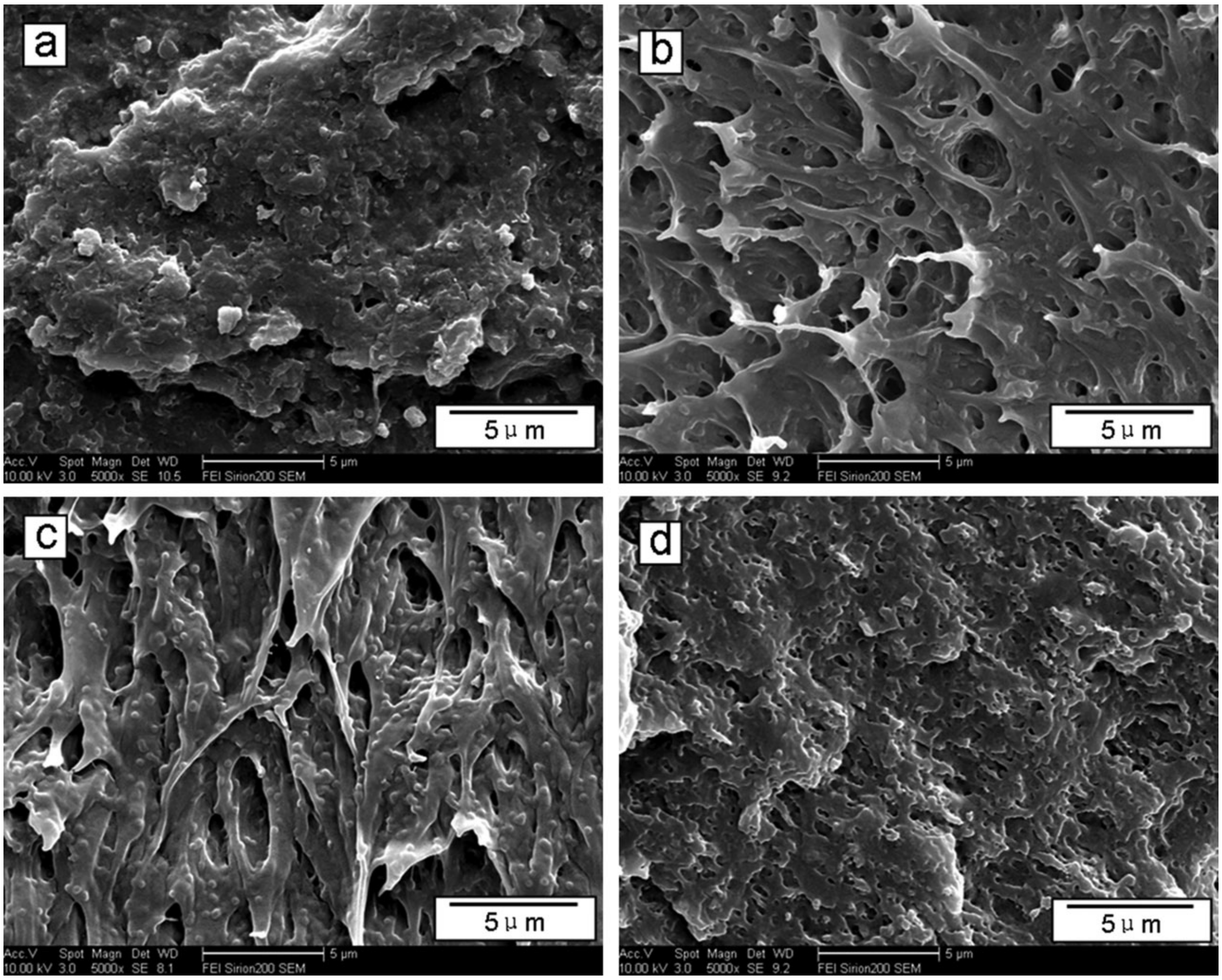

Figure 6. SEM micrographs of fracture surface for the blends: (a) 65 wt %, (b) 70 wt %, (c) 75 wt %, and (d) 80 wt %.

strength reached the highest value of 41.6 kJ/m^2, which was nearly nine times higher than pure PVC, at Is content of 70 wt % and MIS amount of 8 wt %. Impact strength and SEM results showed obvious toughened fracture existed in PVC/MIS. The results of the DMA analysis illustrated that the additive influenced the glass transition temperature of PVC.

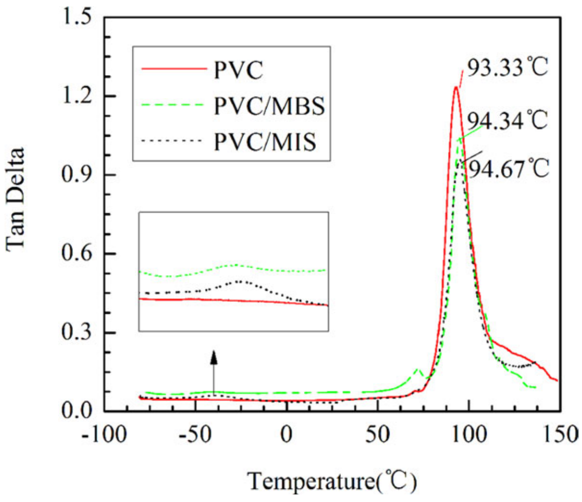

Figure 7. tan δ curves for PVC and the blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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