

Polystyrene/Vinyl Ester Resin/Styrene Thermoplastic Elastomer Composites: Miscibility, Morphology, and Mechanical Properties

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ABSTRACT: Polystyrene/Styrene-Ethylene-Propylene-Styrene/Vinyl Ester Resin (PS/SEPS/VER) blends used as matrix of ultra high molecular weight polyethylene (UHMWPE) fiber-reinforced composites, which included both physical crosslinking points of thermoplastic resin SEPS and chemical crosslinking network of thermosetting resin PS/VER, were prepared by solution blending and hot-molding. Morphology and mechanical properties of the PS/SEPS/VER composites were investigated in this work. The microstructure of PS/SEPS/VER composites observed by means of scanning electron microscopy (SEM) was correlated with mechanical properties. It is worth noting that, stiffness increased sharply with the addition of VER within a certain range. Impact properties verified the structure

that the physical crosslinking points of SEPS were immersed in the chemical crosslinking network of PS/VER. Dynamic mechanical analysis revealed that, incorporation of VER changed the storage modulus and loss tangent. In brief, addition of VER had improved mechanical properties, thermal stability, and fluidity of the composites during processing, indicating a successful result for preparing resin matrix material with outstanding comprehensive performances. Analog map was presented to facilitate better understanding of the special structure of PS/SEPS/VER. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 93–101, 2011

Key words: thermoplastic; thermosetting; composites; dynamic mechanical analysis; mechanical property

INTRODUCTION

Ultra high molecular weight polyethylene (UHMWPE) fiber-reinforced composites are more and more considered for use in manufacture of high-strength ropes, advanced sports products, and protective materials. For these lightweight composites, resin matrix plays an important role in lowering the weight. At present, three types of resins are mainly used as matrix for UHMWPE fiber-reinforced composites, namely polyurethanes (PU),^{1–3} styrene block copolymers (SBC),^{4–6} and vinyl ester resins (VER).^{7–9}

For example, Tang and Teoh¹⁰ reported improved mechanical and thermal properties of UHMWPE fiber-reinforced PU composite. Yu et al.¹¹ investigated the morphology and mechanical properties of styrene-ethylene/butylenes-styrene/high density polyethylene blends and found obvious increase in impact and tensile strength. Cenna et al.¹² analyzed wear mechanism of VER/UHMWPE composite that showed great enhancement in wear resistance to

both hard and soft abrasives. Walsh et al.¹³ studied both PU and VER systems reinforced with UHMWPE fiber and found that both resin matrices made the stress state of composites more uniform than that of the fabrics. But composite laminates with VER outperformed those with PU over the entire range of strain rates. Besides this, some other resins have been studied in recent years. Chen et al.¹⁴ prepared ethylene-methyl methacrylate polymer matrix and UHMWPE composite by gelation/crystallization from solutions.

To ameliorate the embrittlement of highly cross-linked thermosetting resins, modification of thermosetting resins by thermoplastic ones flourished in the past few decades.^{15–19} As pure thermoplastic resins suffer from poor stiffness and combination of advantages of SBC and VER has not been reported, we conceived thermosetting resin modification to thermoplastic ones by incorporating VER. The unsaturated double bonds on both ends of VER could copolymerize with styrene monomer and form chemical crosslinking networks through hot curing. The reaction process was illustrated in Figure 1. VER was known to have many desirable qualities, including mechanical properties comparable with those of epoxy resins, excellent chemical resistance

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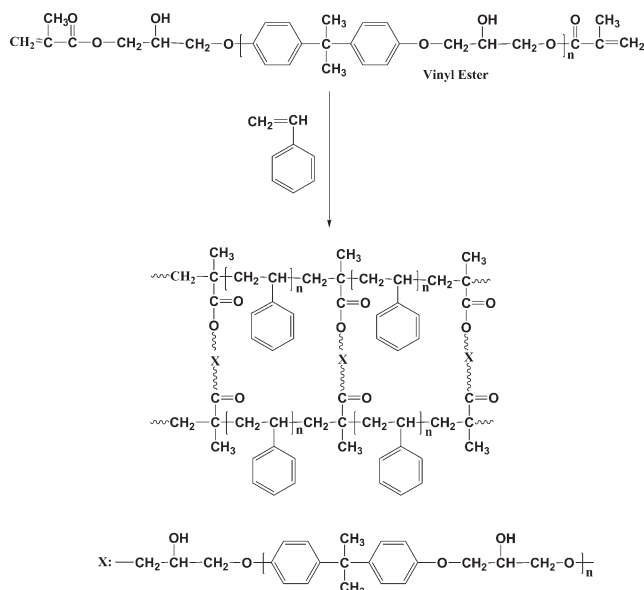


Figure 1 Diagram illustrating the formation of the chemical crosslinking network of PS/VER.

and tensile strength, low viscosity and cost competitiveness.²⁰ Besides, the hydroxyl groups in VER could enhance wettability and adhesion of the resin to the fiber. As a result, great improvements in mechanical properties, rheological properties, and interfacial adhesion could be expected by addition of VER.

In this article, miscibility of St/SEPS/VER blends before hot-molding was first studied combined with a ternary phase diagram of styrene, SEPS and VER for obtaining macroscopic homogeneous PS/SEPS/VER composites through solution blending method. Next, PS/SEPS/VER composites with physical crosslinking points of SEPS and chemical crosslinking network of PS/VER have been prepared through hot-molding. Furthermore, the micro-morphologies and mechanical properties of the composites were investigated. At the same time, dynamic mechanical properties and thermal stability of the composites were studied. Finally, a structure model of the composites was presented to facilitate better understanding of the special structure of PS/SEPS/VER.

EXPERIMENTAL

Materials

All the raw materials used in this study were commercial products. Styrene-Ethylene-Propylene-Styrene (SEPS) tri-block copolymer (SEPTON[®] S2063) with 13 wt % of PS was purchased from Kuraray, Shanghai, China. Vinyl Ester Resin (VER) (V854, Bisphenol A epoxy vinyl ester resin) was supplied by Shanghai Fuchen Chemicals, Shanghai/China; Styrene (CP) provided by Sinopharm Chemical Regent, Shanghai, China; was used as reactive dilu-

ent. BPO (CP) provided by Shanghai Zhong Li Chemical Reagent, Shanghai, China; was used as initiator and purified before use.

Preparation of PS/SEPS/VER composites

Quantitative SEPS resin was first dissolved evenly in styrene at room temperature, followed by adding quantitative VER into the blend. Next an appropriate amount of BPO was added to initiate polymerization of styrene and VER. After vacuum degassing for some time at R.T, the blends were poured into a steel mold and cured in an oven at 120°C for 110 min. Finally, PS/SEPS/VER composite was obtained after demolding, cautiously.

Measurement of viscosity of blends

Viscosities of the blends were obtained using the rotary viscosity tester (NDJ-79) produced by Tongji Experimental Instrument Factory (Shanghai, China).

Characterization of microstructure of composites

PS/SEPS composite was etched by two solvents, one by hexane for 24 h and another by toluene for 5 h, respectively. The composite etched by hexane was softened and the weight loss was 8%, but the one in toluene was fully dissolved. PS/SEPS/VER composite was etched by toluene for 24 h. Loose structure was obtained and the weight loss was 31%. Then, the surface morphologies of these samples after etching and the original ones were all observed through a field emission scanning electron microscope (FESEM by JEOL, model JSM-7401F). All the specimens were gold coated before observation. For the impact samples after impact test, fracture surfaces were also observed by it.

Mechanical properties test

Instron-4465 universal test machine (Instron Corporation, Norwood, Massachusetts) was used to perform tensile and bending tests, according to ASTM D638 and GB2570, respectively. Tensile strength and elongation at break of PS/SEPS/VER composites were obtained. Sample specification for three-point bending test was 11.0 cm × 1.5 cm × 0.3 cm, and stretching rate was 6 mm/min.

According to ASTM D256, Cantilever beam test method was adopted in Notched-Charpy-impact-testing, which was done on the testing machine produced by Model Ray-Ran, UK.

Dynamic mechanical test

Dynamic mechanical test was operated on Dynamic Mechanical Analyzer TA Q800 type (TA Corp., New

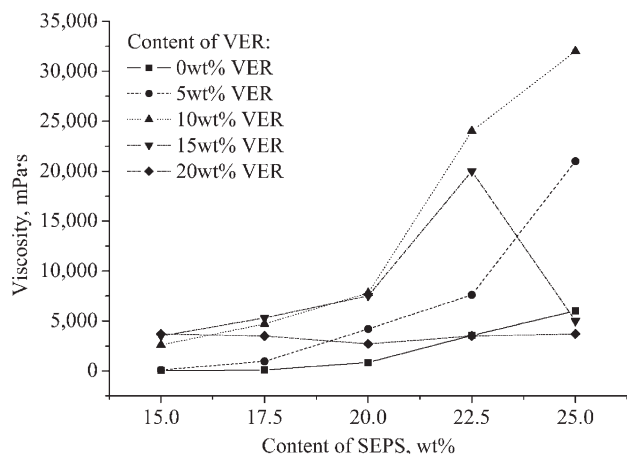


Figure 2 Effect of contents of SEPS and VER on viscosity of St/SEPS/VER blends before hot-molding.

Castle, Delaware), using a tensile mode. Temperature scans were conducted at a heating rate of 3°C/min, ranging from -110 to 120°C, with a fixed frequency of 1 Hz. Sample specification was 60 mm × 10 mm × 3 mm. Testing atmosphere was in nitrogen, with a flow rate of 50 mL/min.

Thermal stability test

Thermal stability was tested on a Thermo Gravimetric Analyzer TA Q2000 type (TA Corp), at a heating rate of 20°C/min, ranging from 40 to 800°C. Testing atmosphere was in nitrogen, with a flow rate of 20 mL/min.

RESULTS AND DISCUSSION

Miscibility of St/SEPS/VER blends before hot-molding

The premise to *in situ* prepare PS/SEPS/VER composites is that thermoplastic resin SEPS can be dissolved evenly in VER and styrene solution before curing. It is very important to form a perfect network between PS/SEPS/VER comparatively after hot-molding, and then excellent comprehensive performances, especially mechanical properties, were obtained. So interaction between SEPS and VER in styrene solution was studied through variations of viscosity of St/SEPS/VER blends before hot-molding, as shown in Figure 2.

From Figure 2, it could be found that when the contents of SEPS were below 20 wt %, relatively little change of blend viscosity appears with the increase of SEPS or VER contents. However, when the contents of SEPS were above 20 wt %, viscosity of the blend increased sharply with the increase of SEPS and meanwhile underwent first increase followed by decline with the increase of VER. Worth

noting was that viscosity reached the highest value for the 10 wt % of content of VER.

It indicated that, when the contents of SEPS and VER were far below that of styrene, viscosity of the blend mainly depended on the content of VER with higher polarity. But when the content of SEPS achieved 20 wt %, SEPS with macromolecular structure promoted viscosity, however, the long molecule chain of SEPS would rather hinder the dispersion of VER in blends, resulting in a lower intermolecular entanglement.

Miscibility of SEPS in VER can also be discussed in terms of ternary phase diagram, as shown in Figure 3. According to preliminary experiments, the solubility limit of SEPS in styrene was within 35 wt %, delineated as apparent upper limit line (B1) in Figure 3. However, when SEPS portion was above 30 wt %, viscosity of St/SEPS blend was quite high, requiring a relatively long period of time for complete dissolution.

For St/SEPS/VER blends, miscibility of these three kinds of components was even more complicated. As incorporation of VER was quite difficult at high viscosity of St/SEPS, the upper limit of SEPS fraction in blends was 25 wt %, as higher than this value processing was impossible. It was depicted as processable upper limit line (B2) in Figure 3. In fact, the weight fraction of VER in the blend of PS/SEPS was also restricted to a certain range. Through a series of solubility experiments, it was found that layered solution occurred when addition of VER was more than 20 wt %, which made it impossible to form composites with homogeneous microstructures during curing. So the blend layered was the basis in the determination of apparent upper limit line (A1) in Figure 3. Moreover, when SEPS was more than 20 wt %, VER fraction was at most 15 wt %, over which the cured composite displayed obvious bubbles on the surface. It was defined as processable upper limit line (A2) of VER. Determination of the

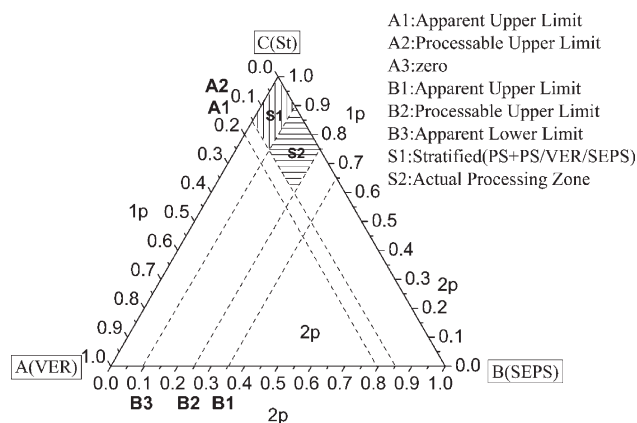


Figure 3 Ternary phase diagram of St/SEPS/VER blends before hot-molding.

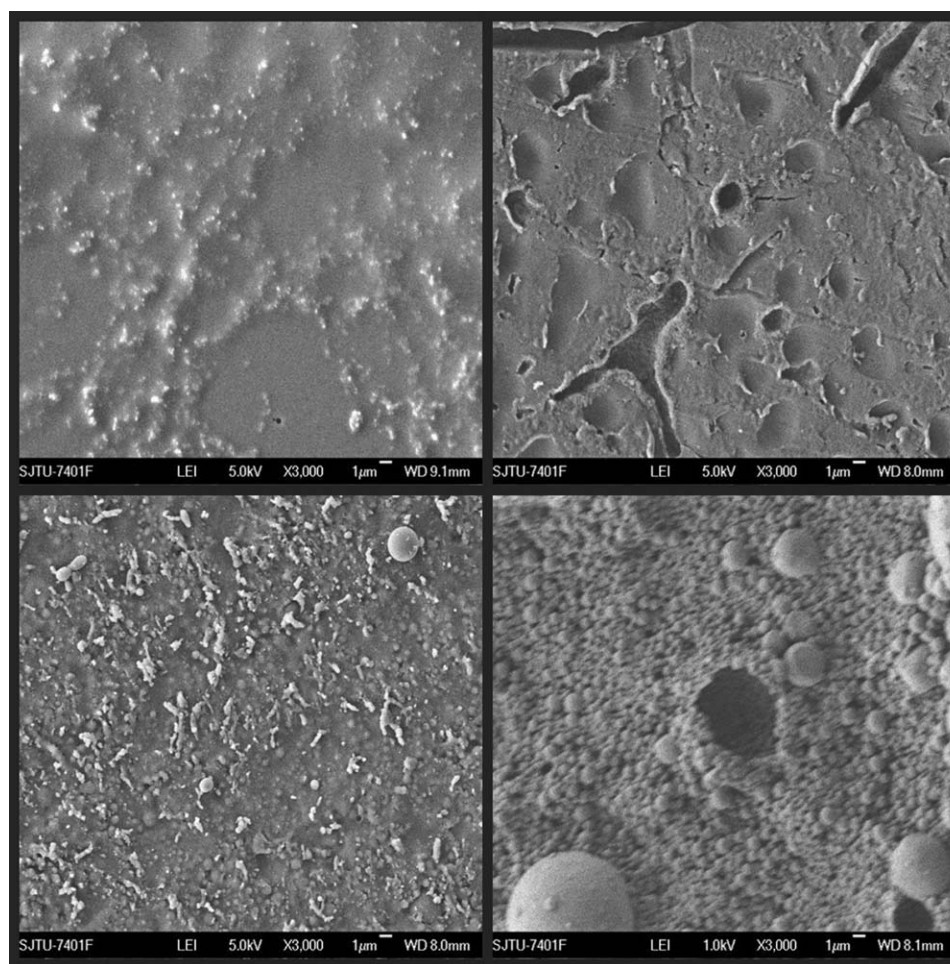


Figure 4 SEM micrographs of PS/SEPS and PS/SEPS/VER composites before and after etching by hexane and toluene, respectively.

lower limit was also based on tri-phase miscibility. VER of 5, 10, or 15 wt % all failed to be miscible with PS/SEPS when the content of SEPS was less than 10 wt %, which exhibited apparent two layers after being left for some time. As a result, two layers also appeared in composites after curing, namely a transparent layer of PS homopolymer and another nontransparent one of PS/SEPS/VER composites. So apparent lower limit (B3) of the weight fraction of SEPS resin was affirmed to be 10 wt %, whereas the weight fraction of VER exhibited no lower limit with A3 being zero. These limit lines built S1 (layered PS/SEPS/VER) and S2 (actual processing zone). In a word, for St/SEPS/VER blends, homogeneous composites could be obtained at SEPS 10–25 wt % and VER 0–15 wt %. All the following discussions are based on the composites within this range.

Viscosity change could also be reflected in the ternary phase diagram. From Figure 3, it was clear that with the increase of VER, its dispersion in St/SEPS got harder and harder, eventually leading to incompatible solutions and thus decreased intermolecular

entanglement. For this reason, the viscosity went up and then down with the increase of VER. For 10 wt % of content of VER addition, the composition just fell in the middle of the actual processing zone, which reflected the best dispersion of VER in blends, leading to the largest degree of intermolecular entanglement.

Microstructure analysis of PS/SEPS/VER composites

The surface morphologies of the cured PS/SEPS etched by hexane and PS/SEPS/VER etched by toluene and their original samples were depicted in Figure 4.

By comparing Figure 4(a,b), it should be pointed out that after etching those white granules dispersed in the matrix has been replaced by dark holes. Considered that SEPS could be dissolved in hexane fully, whereas PS cannot, the result indicated the two components, SEPS and PS, existed in the form of physical blend. Moreover, the data of weight loss of PS/

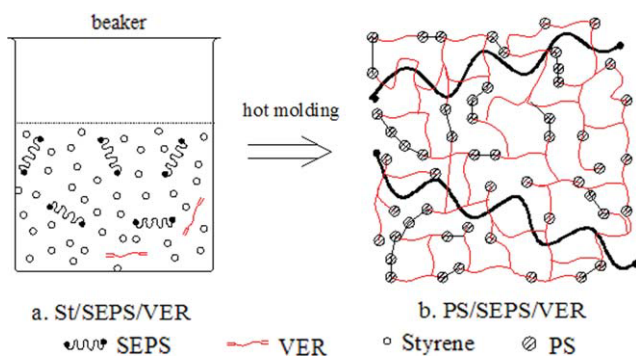


Figure 5 Schematic diagrams of formation of PS/SEPS/VER composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

SEPS sample after etching, which was up to 8 wt %, also validated the conclusion. However, when VER was incorporated in the composites and involved in the construction of the chemical crosslinking network, as indicated in Figure 4(c,d), direct encapsulation of SEPS by the matrix took place. By comparing Figure 4(c,d), it indicated that the sample after etching was obviously different from the one before etching in that dark holes were formed by dissolving out SEPS and some linear PS. As the PS/SEPS composite has been proved to be dissolved in toluene, whereas the chemical crosslinking network of PS/VER could not, PS/VER formed the continuous phase. The appearance of the PS/SEPS/VER composite after etching also permitted the reasonable conclusion reached here. It was first swelled by toluene and then after being dried in the oven the left-over structure with pores in it collapsed. The weight loss after etching by toluene was 31 wt %, which indicated that SEPS and some linear PS that was not crosslinked with VER were dissolved. Hence, a valued conclusion could be deduced that the special structure with the physical crosslinking points of SEPS dispersed in the chemical crosslinking network of PS/VER had been formed. This analysis was also consistent with the conclusions obtained by other authors.^{21–23} According to these references, SEPS was characterized by physical crosslinking points at room temperature as T_g of the PS segment in SEPS was 100°C and PS/VER could be cured to form chemical crosslinking network. Also, there were no macro-phase-separation observed in St/SEPS/VER blends before curing, there would be a kind of interpenetrating network at R.T after curing.

Figure 5 depicted the schematic diagram of the special structure of PS/SEPS/VER composite. The molecular chain of linear SEPS interpenetrated the chemical crosslinking network of PS/VER. The addition of VER yielded highly rigid and crosslinked structures, responsible for improvement in stiffness and thermal stability discussed in detail later.

Bending properties and stiffness of PS/SEPS/VER composites

In this work, thermosetting resin VER was added in the hope of increasing stiffness of the SEPS-containing composite. The result obtained from Figure 6 agreed well with this idea. When the mass fraction of SEPS was below 17.5 wt %, addition of VER brought great increase of Young's modulus. When the content of SEPS was 15 wt %, addition of 15 wt % of VER increased Young's modulus by 800%.

In Figure 6, the composite demonstrated increased Young's modulus at $w_{SEPS} < 17.5$ wt %, with the increase of VER. It could be explained by the modulus formula:

$$E = \Delta P \frac{l_0^3}{4bd^3\Phi}$$

where ΔP represents load of the composite. Φ refers to bending deformation. l_0 , b , d are length, width, and thickness, respectively. In this formula, $\Delta P/\Phi$ is variable. For specimen at $w_{SEPS} < 17.5$ wt %, the composite yielded highly rigid and chemical crosslinked structures with the increase of VER content, giving rise to the small Φ and high E values. However, with the increase of SEPS, Φ rose and reached an extreme point, the modulus decreased and eased up accordingly. When w_{SEPS} was above 20 wt %, addition of VER exerted little influence on modulus. At $w_{SEPS} < 20$ wt %, the influence of VER on modulus was reflected on the decrease of Φ .

Tensile properties of PS/SEPS/VER composites

With the variety of thermoplastic and thermosetting contents in PS/SEPS/VER composites, tensile properties indicated some typical characterization of different materials, from flexible elastomer to brittle

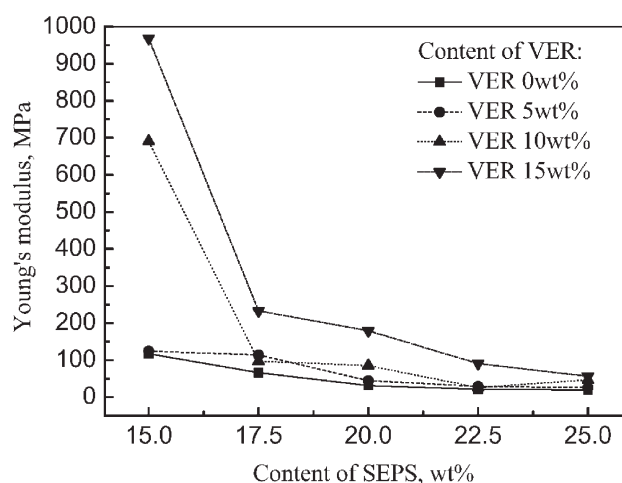


Figure 6 Effect of contents of SEPS and VER on Young's modulus of composites.

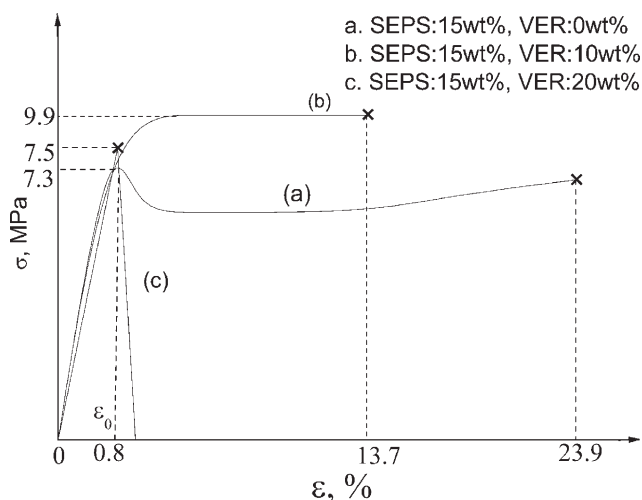


Figure 7 Schematic diagrams of three typical tensile behaviors of PS/SEPS/VER composites.

plastics. Schematic diagram of three typical tensile behaviors determined on experimental data was presented in Figure 7.

Figure 7(a) shows a typical yield phenomenon, as there was no VER. During the tensile process, white craze occurred at the yield point after which relative stable tensile behavior characterized by toughness with a slight decline in the curve was shown. Near the tensile failure point, the stress began to increase till fracture. Elongation at break in this case was the largest, being 23.9%. It should be noted that after fracture, two halves of the specimen restored to their original state, without leaving a stretch mark to be seen.

With 10 wt % addition of VER, the yield point blurred and the curve leveled off, even with a slight decline. It revealed that VER promoted a solid chemical crosslinking network after curing that restricted change in conformation of the physical network of SEPS. What was more, as VER provided rigid support for the physical crosslinking points, tensile stress was also increased. But elongation at break was reduced to 13.7% [see Fig. 7(b)].

Figure 7(c) suggested that when SEPS was 15 wt % and VER was 20 wt %, the brittle fracture occurred before the yield point. Elongation at break was reduced to 0.8%. This was attributed to the brittle PS/VER chemical crosslinking network that led to the decline in toughness. Introduction of the chemical crosslinking network restricted mobility of molecules, making the composite almost lost tensility.

In Figure 7(a), the maximum tensile strength may arise either at the yield point or fracture. Generally, for PS/SEPS system, the ductile fracture point often constituted as the maximum tensile strength, whereas it occurred before the yield point with the increase of VER content in the system, which was

characterized by brittle fracture [see Fig. 7(c)]. Figure 7(b) showed that, when the mass ratio of VER/SEPS fell between that of Figure 7(a,b), the maximum tensile strength was obtained at the yield point.

Therefore, it can be anticipated that within the actual processing zone discussed in the ternary phase diagram of St/SEPS/VER, materials of different kinds of mechanical properties can be tailored for desired applications by way of adjusting and controlling contents of VER and SEPS in the composite.

Impact behavior of PS/SEPS/VER composites

Because *in situ* polymerization was adopted in fabricating the special polymer network, that is, introducing physical crosslinking points of SEPS, which contained noncrystallized rubber chain into the cured chemical crosslinking network of PS/VER, the composite demonstrated outstanding toughness. It was generally believed that the EP rubber chain segment in SEPS promoted impact behavior. For the chemical crosslinking network of PS/VER, impact strength was related to its content. Synergy between the two crosslinking structures decided the trend of impact strength. Figure 8 suggest that impact strength was on the rise as SEPS content increased. When w_{SEPS} was below 20 wt %, it had little effect on impact strength. However, when w_{SEPS} was above 20 wt %, the increased EP chain content had appreciable effect on impact strength, making SEPS responsible for the sharp increase of impact strength at the macro level.

Further examination of Figure 8 revealed that the system of SEPS and PS without VER displayed the most obvious upward trend, which reflected the effect of SEPS on impact strength. VER had a deleterious effect on impact strength, which could be

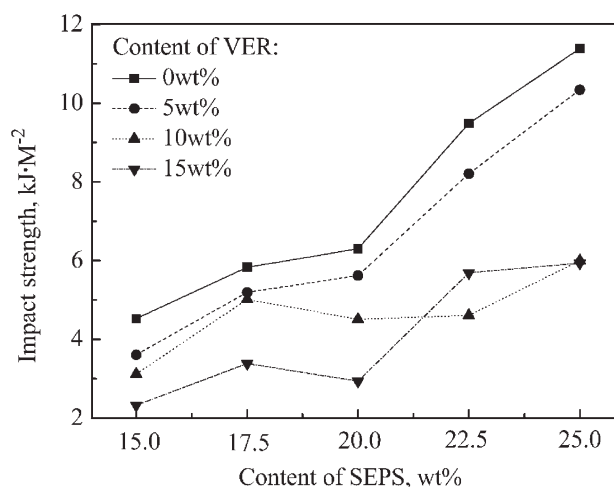


Figure 8 Effect of contents of SEPS and VER on impact property of PS/SEPS/VER composites.

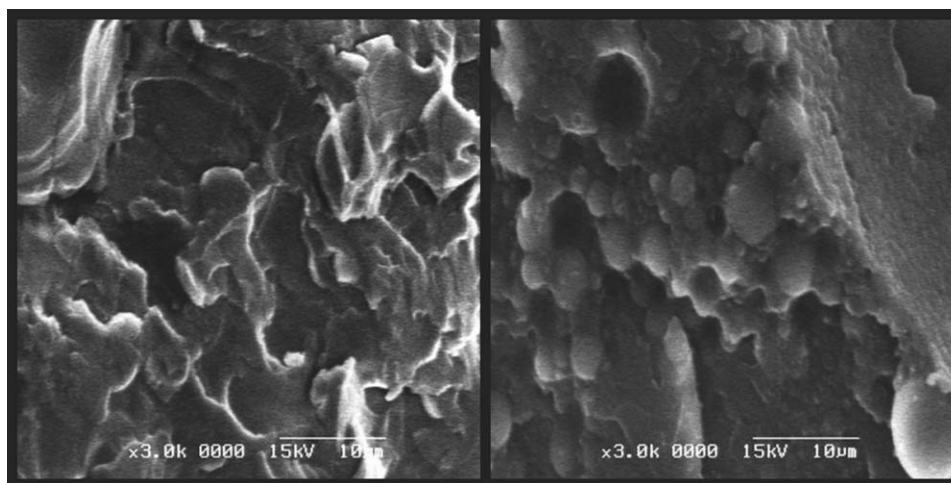


Figure 9 SEM micrographs of cross section of PS/SEPS/VER composites (3000 \times).

interpreted that the cured chemical crosslinking network of VER/PS restricted mobility of chain segments. When contents of SEPS and VER were both high, especially when VER reached 15 wt %, increase of SEPS from 22.5 wt % to 25.0 wt % had almost no effect on impact strength. The behavior was attributed to the relative order of the dispersed system that was brought about by mutual repulsion of the polar groups of VER when the viscosity was quite high. Therefore, the cured chemical crosslinking network of PS/VER was dominant in showing impact resistance whereas the effect of SEPS on impact resistance was relatively low.

In accordance with further observation of the impact cross section, a comparison of Figure 9(a,b) denoted that the composite in which VER was added yielded corrugated interfacial fracture folds with granular gaps in exposure to impact. The addition of VER changed the original dispersion state of SEPS. Through compulsive dispersion of SEPS and

VER, the special structure of SEPS interpenetrating PS/VER was formed by *in situ* polymerization. In this manner, VER provided rigid support, whereas SEPS enhanced toughness at impact. Those spherical distributed particles in Figure 9(b) were capable of absorbing impact energy during fracture.

Dynamic mechanical analysis (DMA) of PS/SEPS/VER composites

The DMA has been increasingly used for the study and characterization of the mechanical properties of composite materials in particular, owing to the dynamic loading situations frequently found where composites are used.

For polymers, storage modulus represents elasticity out of viscoelastic behaviors, reflecting rigidity of the material. From Figure 10(a), it could be seen that storage modulus at low temperature was related to the content of SEPS. This was because at low

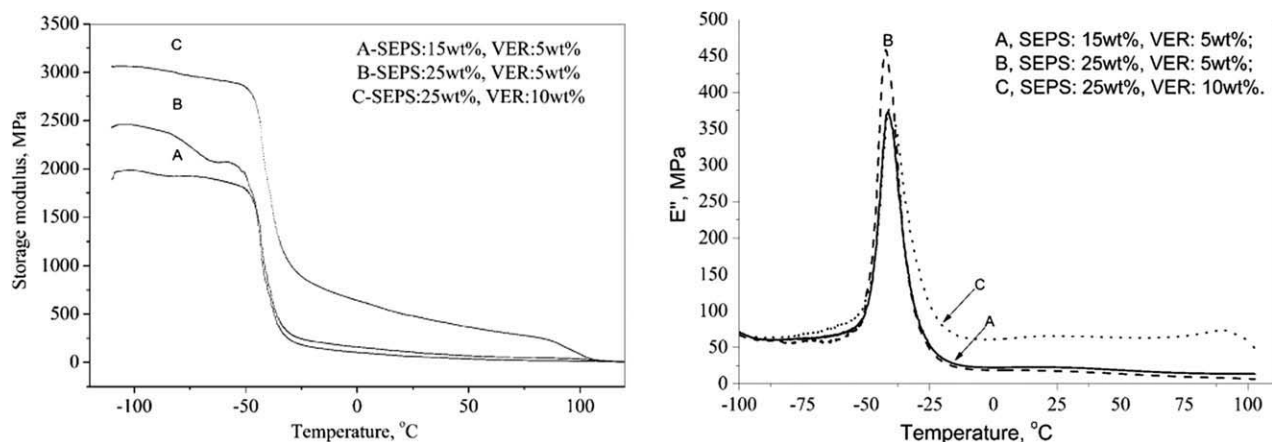


Figure 10 Storage modulus and loss modulus of PS/SEPS/VER composites.

temperature, frozen level of the flexible EP chain segment determined mechanical properties of the composite. Once the external temperature exceeded T_g of the EP chain segment, storage modulus underwent a sharp decrease by two orders of magnitude to a rather low level, making the composite exhibit low stiffness and namely high elasticity.

A comparison between lines B and C in Figure 10(a) revealed that the cured VER could bring about a significant improvement in storage modulus and enhance stiffness of the composite as a result. As shown in the figure, an increase of only 5 wt % of VER facilitated tremendous upgrades within the whole temperature range.

However, loss modulus represents viscosity out of viscoelastic behaviors, reflecting flexibility of the material. The peak at -40°C was T_g of EP segment. A comparison of the three lines in Figure 10(b) revealed that when VER content was constant, increase of SEPS, that is, more EP segments, lifted loss modulus by 30% at -40°C . After T_g , as the crosslinking points of SEPS was disbanded, loss modulus of lines A and B were similar. Moreover, when SEPS content was constant, the increase of VER had indeed an effect on flexibility of the material. As we can see that line C was above lines A and B by about 50 MPa. For noncrystallized polymers, loss modulus was associated with order level. The cured VER characterized by rigid groups such as benzene rings in the main chain and infinite molecular weight in theory constrained molecular motion of other segments to a great degree, making their movement more difficult. Thus, loss modulus was increased.

Thermostability of PS/SEPS/VER composites

With respect to potential applications of composites, including aviation, construction, and individual protection, to name a few, thermal stability of composites is an important index.

In accordance with previous study, low content of SEPS did not affect thermal stability of the composite. However, significant change of thermal stability of the composite took place in the case of VER content variation, as indicated in Figure 11, from which we could see that when the content of VER increased from 0 to 20 wt %, decomposition temperature increased from 434 to 440°C . This may be explained by the addition of VER characterized by higher polarity which enlarged intermolecular forces. Thus, thermal stability was increased. It should also be noted that as PS/VER formed the continuous phase, there was only one thermogravimetric step in the figure, which indicated that the special structure with the chemical crosslinking net-

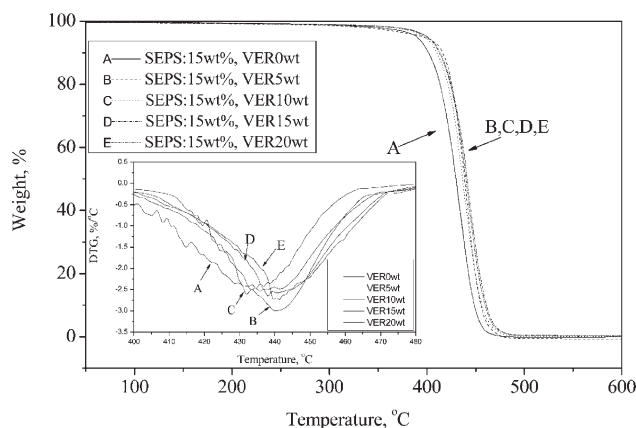


Figure 11 Effect of contents of VER on heat stability of PS/SEPS/VER composites.

work of PS/VER and the physical crosslinking points of SEPS was formed.

CONCLUSIONS

A series of PS/SEPS/VER composites characterized by special structures were prepared by solution blending and hot-molding methods. The actual processing zone was built by those limit lines that were determined through a number of preliminary solubility experiments.

In accordance with SEM observations, SEPS was dissolved out in both PS/SEPS and PS/SEPS/VER composites, leaving dark holes on the surface. The chemical crosslinked PS/VER constituted the continuous phase. The structure having both physical crosslinking network of SEPS and chemical crosslinking network of PS/VER had formed at R.T.

It was well accepted that the addition of VER led to the blurring of the yield point and the brittle fracture because of the rigid chemical crosslinking network after curing restricted conformation change of SEPS. The conclusions that VER increased stiffness of the SEPS-containing composite could be drawn. When the mass fraction of SEPS was 15 wt %, addition of 15 wt % of VER increased Young's modulus by 800%. It was evidenced by impact behavior that chemical crosslinking network of PS/VER provided rigid support, whereas the molecular chains of SEPS enhanced toughness. Synergy between the two crosslinking networks decided the trend of impact strength.

DMA analysis revealed that incorporation of VER changed the storage modulus and loss tangent. VER brought about a significant improvement in storage modulus of the composite. An increase of only 5 wt % of VER facilitated tremendous upgrades.

Besides, the addition of VER was accompanied by a significant influence on thermal stability of the composite. Addition of VER characterized by higher

polarity enlarged intermolecular forces and lifted decomposition temperature accordingly. Formation of the chemical crosslinking network was also responsible for the single thermogravimetric step in Figure 11.

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