Rheological, Mechanical and Morphological Properties of Thermoplastic Vulcanizates Based on High Impact Polystyrene and Styrene-Butadiene Rubber

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ABSTRACT: Thermoplastic vulcanizates (TPVs) based on high impact polystyrene (HIPS)/styrene-butadiene rubber (SBR) blends were prepared by dynamic vulcanization technique. The rheological, mechanical and morphological properties of the dynamically vulcanized blends were investigated systematically. As determined by capillary rheometer, the apparent viscosity of the blends decreases as the shear rate increases, indicating obvious pseudoplastic behavior. At low shear rate, the apparent viscosity of these blends is considerably higher than that of neat HIPS and decreases with the increase of HIPS concentration. The increase of HIPS content in the dynamically vulcan-ized blends contributes to the increase of tensile strength and hardness properties, while elongation at break and tensile set at break reach a maximum at 30 and 50 wt % of the HIPS content, respectively. The etched surfaces of the HIPS/SBR TPVs were investigated using field-emission scanning electron microscopy, the morphological study reveals continuous HIPS phase and finely dispersed SBR elastomeric phase in the TPVs. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2523–2529, 2010

Key words: polystyrene; styrene-butadiene rubber; blends; elastomers; dynamic vulcanization

INTRODUCTION

Thermoplastic elastomers (TPEs) are known as a class of polymeric materials with elastic and mechanical properties similar to those of conventional vulcanized rubbers. They can be processed in a molten state as a thermoplastic polymer. Thermoplastic vulcanizates (TPVs), as a special case of TPEs, are produced via dynamic vulcanization of blends of a rubber and a thermoplastic polymer.[1–3] Dynamic vulcanization is the procedure in which curing agents are used to crosslink an elastomer *in situ* during its mixing with molten plastics, which was first described by Gessler[4] in 1962 and further developed by Fisher,[5] Coran and Patel,[6] and Sabet.[7] Morphologically, the resulting TPVs are characteristic of finely dispersed, micrometersized, crosslinked rub-ber particles distributed in a continuous thermoplastic matrix.[8–11]

Compared with those blends comprising of uncured or slightly crosslinked components, dynamic vulcanization possesses significantly improved mechanical properties that can be attributed to the stabilized morphology of rubber particles resulting from crosslinking. Many papers have been published dealing with the mechanical properties and morphology of TPVs.[12–14] Generally, the properties of TPVs exceed those of block copolymer TPEs. Because of their unique characteristics, TPVs play a very important role in the applications of automotives, buildings and constructions, wires and cables, etc.

Although TPVs have been extensively used in industry, few papers have been published to address their rheological behavior. The first investigation on the rheological properties of TPVs was performed by Goettler et al.[15] In recent years, the melt flow behavior of TPEs produced by the dynamic vulcanization of rubber/plastic blends has received much attention, and the rheological behavior of the TPVs has been studied using plate–plate and capillary rheo-meters.[16–20] Usually, TPVs exhibit non-Newtonian viscosity and the molten TPVs behave like the particle filled polymer melts. Experiments have also been carried out to characterize the morphology of TPVs based on the different rubber–plastic blends.[21–24]

In the last two decades, conventional PP/EPDM TPEs and, especially, PP/EPDM TPVs have been extensively studied because of their commercial importance.[25] Commercial TPVs contain large quantities of extender oil to improve their processability and decrease their hardness. The blends of natural rubber, butyl rubber, or nitrile rubber with either PP or polyethylene were less studied. Literature say nothing of the dynamic vulcanizates based on the mixture of styrene-butadiene rubber (SBR) and thermoplastic materials.

In this article, we reported the preparation of TPVs based on the blends of high impact polystyrene (HIPS) and SBR via dynamic vulcanization. The HIPS has additional rubber (polybutadiene), moreover, the small amount of polybutadiene which is grafted to the polystyrene in HIPS could be compatibilizing the SBR/HIPS compositions, which could give rise to greatly superior materials in comparison with the SBR/PS TPVs prepared by Coran et al.[2] Morphology of the dynamically vulcanized HIPS/SBR blends were studied using field-emission scanning electron microscopy. The rheological and the mechanical properties of the dynamically vulcanized blends were investigated systematically as a function of the HIPS/SBR blend composition.

EXPERIMENTAL

Materials

SBR rubber, 1502 type (styrene content, 30 wt %), was commercially manufactured by synthetic rubber factory of Qilv Branch, China Petrochemical Co., Zibo, China. HIPS was supplied by the Shanghai SECCO Petrochemical Co., Shanghai, China. The HIPS was injection grade 622P with a melt flow index (MFI) of 4.8 g/10 min at 200°C. The polybutadiene content in the graft copolymer was 7.5 wt %. Tetramethylthiuram disulfide (TMTD) and N-cyclohexyl-2-benzothiazole sulfenamide (CZ) were used as accelerators and manufactured by Northeast Auxiliary Chemical Industry Co., Hebei, China. Sulphur was used as a vulcanization agent, obtained from Hengye Zhongyuan Chemical Co., Beijing, China. Zinc oxide (ZnO) was used as an activator, which was obtained from NewLe Qinshi Zinc Co., Xinle, China. Stearic acid was used as an activator, obtained from Wanyou Co., Zibo, China, and N-isopropyl-N′-phenylenediamine (Antioxidant 4010NA) was used as an antioxidant, which was obtained from Shengao Chemical Co., Caoxian, China.

Preparation of dynamically vulcanized HIPS/SBR blends

Commercially available SBR rubber and HIPS were used for the TPVs. The concentrations in crosslink SBR system were expressed in parts per hundred part of rubber by weight (phr). The sulfur-containing accelerating system consisted of the following: 100 phr SBR, 2.0 phr CZ, 0.2 phr TMTD, 1.0 phr sulfur, 1.5 phr stearic acid, 5.0 phr ZnO, 2.0 phr 4010NA.

The dynamically vulcanized HIPS/SBR blends were produced via a two-step mixing process. In the first step, the preblends containing SBR and the crosslink ingredients were compounded in a two-roll mill at room temperature. After 3 min of mixing time, the preblends were removed from the mixer. In the second step, the TPVs compounds were prepared, by melt-mixing the SBR preblends with the HIPS resin using a Brabender PLE 331 plasticorder (Brabender Gmbh, Germany). The mixer temperature was kept at 165°C with a constant rotor (cam-type) speed of 80 rpm. The HIPS/SBR weight ratio varied from 70/30 to 20/80. In detail, first, the required quantity HIPS resin was charged into the mixer and allowed to melt. After 2 min, the SBR based preblend was added. The mixing was continued for another 8 min to allow the dynamic vulcanization. Finally, the molten compound was removed from the mixer and then passed through a cold two-roll mill to obtain a sheet about 2 mm thick. The sheet was cut and pressed for 10 min in a compression-molding machine at 180°C. Aluminum foil was placed between the molded sheet and the press plates. The sheet was then cooled down to room temperature under pressure. Test specimens were die-cut from the compression-molded sheets and used for testing after 24 h.

Characterization

For the measurement of tensile properties, dumbbell-shape specimens were prepared according to ASTM D412. The tearing strength was tested according to ASTM D624 using the unnotched 90° angle test pieces. Both tensile and tearing tests were performed on a universal testing machine (AI-7000M, Taiwan Gaotie Technology, China) at a crosshead speed of 500 mm/min. The Shore A hardness was determined using a hand-held Shore A Durometer according to ASTM D2240. All tests were carried out at 23°C. The average value was calculated for 5 test specimens.

The rheological behavior of HIPS and the dynamically vulcanized HIPS/SBR blends was measured using Rosand Precision Rheometer (Bohlin Instrument, Britain) under Double-bore experiment mode. The L/D ratio of the capillaries were 16/1 and 0, respectively. The experiments were carried out at 200°C. The results were processed by the software afforded by Bohlin Instrument, and all the rheological data obtained were subjected to Bagley and Rabinowitch calibration.
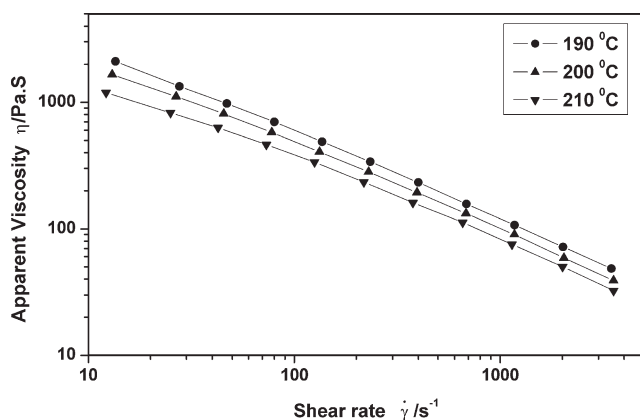
Figure 1 Shear rheology curves of neat HIPS at various temperature.

Morphological study was carried out using field-emission scanning electron microscopy (FE-SEM, JEOL-6700F, Japan Electron Co.). For the etched specimens, the HIPS phase was extracted by immersing the blends into xylene for 3 min. Then the samples were dried in vacuum oven at 40°C for 3 h. The etched surfaces and the fracture surfaces of the specimens were sputtered with thin layers of gold and probed using FE-SEM.

RESULTS AND DISCUSSION

Rheological behavior of the dynamically vulcanized HIPS/SBR blends

Figure 1 shows the shear rheology behavior of neat HIPS at different temperatures. The neat HIPS exhibits notable pseudoplastic behavior. The apparent viscosity decreases significantly with the increasing shear rate, especially at low shear rate, indicating high orientation degree of HIPS chains along the shear direction even at relatively low shear rate. However, the increase of shear rate has minimal effect on the apparent viscosity at shear rates above 500 s^{-1}. Compared with the influence of shear rate on the rheology behavior, increasing temperature has relatively weak impact on the apparent viscosity of the neat HIPS melt.

The shear rheology curves for the dynamically vulcanized blends with different HIPS/SBR weight ratio are presented in Figure 2. The apparent viscosity significantly decreases with the increasing shear rate, revealing pseudoplastic nature of these specimens. The apparent viscosity of the dynamically vulcanized HIPS/SBR blends is much greater than that of neat HIPS, especially at low shear rate, indicating strong interface interaction between the thermoplastic HIPS and the crosslinked SBR phase.

As shown in Figure 2, the apparent viscosity substantially increases as the SBR content increases. The apparent viscosity of the HIPS/SBR blends decreases
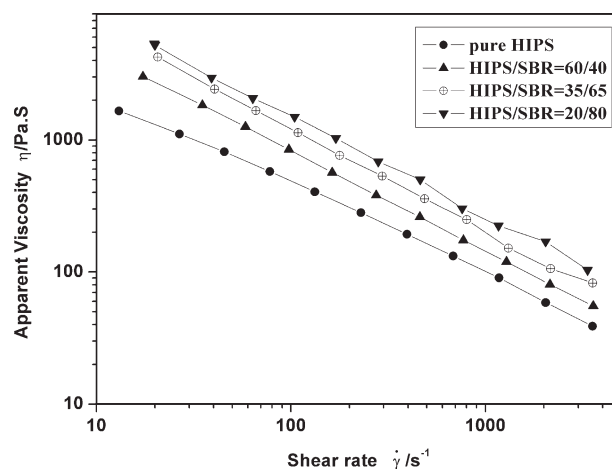
sharply with the increase of shear rate. Their rheology curves tend to merge at the shear rate greater than 500 s^{-1}. Usually, the structure of polymer blends determines rheological behavior. A major difference between the melts of neat polymer and filled polymer composites is understandable. The flow of neat polymer is accompanied by the irreversible deformation, which facilitates the flow. However, in the composite case, undeformable particles of the fillers hinder the flow of the polymer matrix.[26] The melt of dynamically vulcanized HIPS/SBR blends can be considered as a suspension system. The crosslinked dispersed SBR particles are less deformable and retain their morphology in the blend melt even at high shear stress, leading to higher viscosity than that of neat HIPS melt. Furthermore, under high shear stress, the breakdown of the physical crosslinked three-dimensional network structure formed by these SBR particles would cause a significant decrease of viscosity, as can be seen in Figure 2.
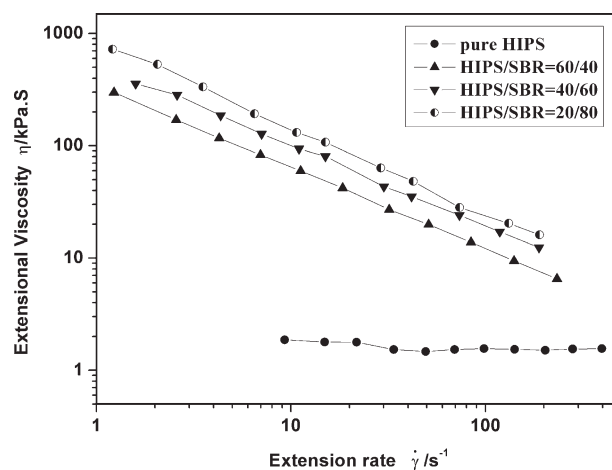

Figure 2 Shear rheology curves of neat HIPS and dynamically vulcanized HIPS/SBR blends at various weight ratio.

Figure 3 Extensional flow curves of neat HIPS and dynamically vulcanized HIPS/SBR blends.
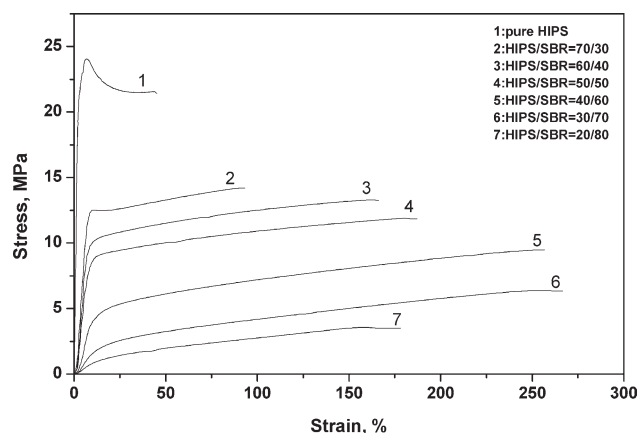
Figure 4 Stress–strain curves of HIPS and dynamically vulcanized HIPS/SBR blends.

The relation between the extensional viscosity of the dynamically vulcanized HIPS/SBR blends and the extension rate is shown in Figure 3. The extensional viscosity of neat HIPS is almost not changed throughout the entire range of extension rate, indicating the relatively stable melt structure. In contrast to neat HIPS melt, the dynamically vulcanized HIPS/SBR blends show distinctly different extensional rheology behavior. The extensional viscosity decreases greatly with the increasing extension rate. The extensional rate has minor effect on the extensional viscosity when the extension rate exceeds 50 s^{-1}. It is noteworthy that the spatial distribution of crosslinked SBR particles in the dynamically vulcanized blends is similar to a three-dimensional network in the HIPS matrix. The viscosity of the blends is influenced by the structural network formed by these SBR particles. It has been reported that the formation of the continuous three-dimensional network in TPVs was constrained effectively, even at low shear rate, resulting in high viscosity.[17] However, the breakdown of the networks at the high extensional rate caused a dramatic decrease in extensional viscosity.

Mechanical property of the dynamically vulcanized HIPS/SBR blends

Figure 4 shows the stress–strain behaviors of neat HIPS and the dynamically vulcanized HIPS/SBR blends at different weight ratio. The stress–strain

traces show drastic difference with the increasing SBR content.

For the neat HIPS, a notable yield point immediately followed by fracture is observed. For the HIPS/SBR blend with 70/30 weight ratio, a yield peak is also observed but the yield strength is lower than that of the neat HIPS because of the presence of elastomeric SBR particles in HIPS matrix. After the yield point, tensile stress slightly decreases, followed by strengthening, indicating that the blend behaves as to a typical plastic with improved toughness. With the increase of the SBR content, the yield peak is absent at the 60/40 weight ratio. Initially, a dramatic increase in tensile stress and modulus, is also observed. Upon further deformation, the slope of the curve decreases. Then the stress increases almost linearly with strain until fracture occurs. Interestingly, no neck formation is found with the increasing SBR content. According to the remarkable difference of the stress–strain diagrams in Figure 4, we can determine that the dynamically vulcanized HIPS/SBR blends can be attributed to TPVs merely only when the HIPS/SBR weight ratio is in the range 40/60–20/80, where the dynamically vulcanized blends possess the representative elastomer character.

The mechanical properties results and standard deviations of the dynamically vulcanized HIPS/SBR blends at various blend ratios are presented in Table I. Tensile strength, shore A hardness, elongation at break, tensile set at break and tearing strength of the dynamically vulcanized HIPS/SBR blends are shown in Figure 5–7, respectively. As can be seen in Figure 5, increasing the loading of HIPS in the blends leads to improved tensile strength and hardness, especially at HIPS content less than 50 wt %, implying the HIPS content is a major factor determining the tensile strength and hardness.

The elongation at break (Fig. 6) decreases significantly with the increasing HIPS content when the HIPS content exceeds 30 wt %. HIPS behaves as a hard and brittle thermoplastic polymer that breaks at relatively low strain when the tensile test is performed at a high crosshead of 500 mm/min. In addition, the elongation at break at weight ratio of 20/80 is relatively low, presumably because of nonuniform distribution of the crosslinked SBR particles in the HIPS matrix. The tensile set at break increases

TABLE I
Mechanical Properties of Dynamically Vulcanized HIPS/SBR Blends

HIPS/SBR weight ratio	20/80	30/70	40/60	50/50	60/40	70/30
Tensile strength (MPa)	3.6 ± 0.16	6.2 ± 0.12	8.5 ± 0.21	11.8 ± 0.28	12.9 ± 0.33	13.5 ± 0.21
Shore A hardness	73.0 ± 0.60	82.6 ± 0.84	93.5 ± 0.87	95.4 ± 1.69	96.4 ± 0.98	96.8 ± 0.64
Elongation at break (%)	184.7 ± 4.70	267.2 ± 5.90	236.1 ± 8.76	192.4 ± 14.42	159.3 ± 4.67	74.2 ± 3.85
Tensile set at break (%)	10.8 ± 0.52	22.0 ± 0.64	37.5 ± 1.36	43.0 ± 2.10	34.0 ± 1.75	14.0 ± 0.87
Tear strength (KN/m)	25.4 ± 0.47	38.4 ± 2.74	53.2 ± 1.76	61.3 ± 1.69	77.2 ± 2.16	85.8 ± 2.99

Figure 5 Effect of HIPS content on tensile strength and Shore A hardness of dynamically vulcanized HIPS/SBR blends.

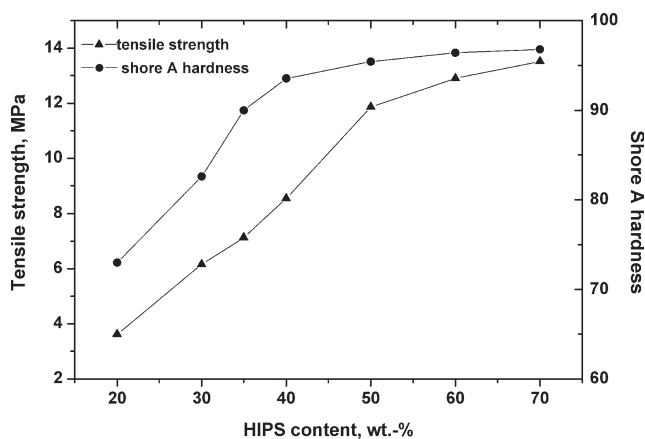**Figure 7** Effect of HIPS content on tear strength of dynamically vulcanized HIPS/SBR blends.

markedly with the increasing HIPS loading when the HIPS content is below 50 wt %, where the dynamic vulcanized HIPS/SBR blends behave as TPVs. Generally, the dynamic vulcanizates exhibit large reversibility and small residual strains.[27] The elastomeric crosslinked SBR particles dispersed in the HIPS matrix enable the HIPS/SBR blends to elastically recover from a highly deformed state. As a result, higher SBR loading lead to lower tensile set at break, as shown in Figure 6. This occurs at concentrations below 50 wt % HIPS. Keeping Figure 4 in mind, it is clear that the blends at HIPS content greater than 50 wt % possess the representative thermoplastic behavior with improved toughness, which exhibit evident characteristic of hardness, especially at high tensile speed, leading to the relatively lower elongation at break and lower tensile set at break.

The HIPS content affects the tear strength markedly. As shown in Figure 7, the tear strength presents linear increase with the HIPS content, indicating a remarkable reinforcing effect of HIPS.
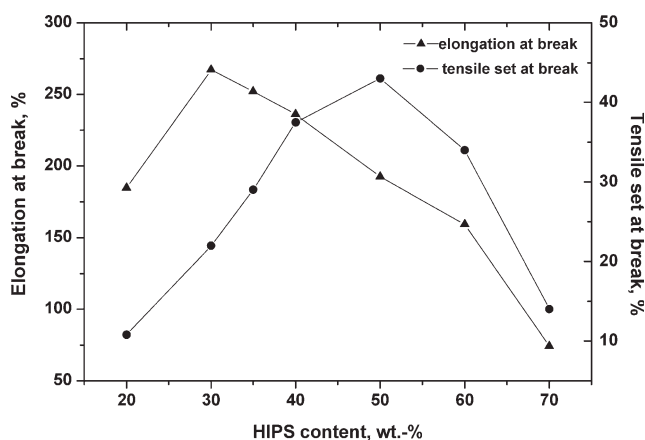
Fracture morphology and microstructure of HIPS/SBR blends prepared by dynamic vulcanization

FE-SEM micrographs of the tensile fracture surfaces of HIPS/SBR blends prepared by dynamic vulcanization are shown in Figure 8. Figure 8(a) shows the tensile fracture surface of the HIPS/SBR blend at 70/30 weight ratio. Rough fracture surfaces indicate ductile fracture behavior. The obvious tearing strips on the fracture surface show that the specimen is a representative thermoplastic with improved toughness, consistent with the tensile analysis based on Figure 4. Significant fracture deformation is also observed in Figure 8(b). However, no notable tearing strip is found. The fracture surface is relatively smooth compared with that in Figure 8(a). The stress–strain curves in Figure 4 have shown that the specimen for Figure 8(b) is a typical elastomer. That is, the HIPS/SBR blend with 40/60 weight ratio is TPVs. Upon elongation, the thin thermoplastic layers at the equator of the rubber particles are subjected to plastic yielding; upon relaxation, they are drawn back by the elastic rubber domains effectively.[28,29] Therefore, the HIPS/SBR TPVs show strong elasticity and less permanent set during the tensile experiment, consistent with the fracture morphology in Figure 8(b) and the lower tensile set at break in Figure 6.

The etched surfaces of the HIPS/SBR TPVs based on 40/60 ratio blend are shown in Figure 9. Many whisker-like particles are observed on the etched surface of the HIPS/SBR TPVs, as shown in Figure 9(a), apparently, these particles are crosslinked SBR. Figure 9(b) shows the morphology of the crosslinked SBR particles at higher magnification. A mass of thin strip-like SBR particles with average diameter of 2 μm are uniformly dispersed in the continuous HIPS matrix. During the dynamic vulcanization, the viscosity of the SBR phase increased quickly because of the initiation of crosslink reaction and the SBR phase was gradually broken down into dispersed

Figure 6 Effect of HIPS content on elongation at break and tensile set at break of dynamically vulcanized HIPS/SBR blends.
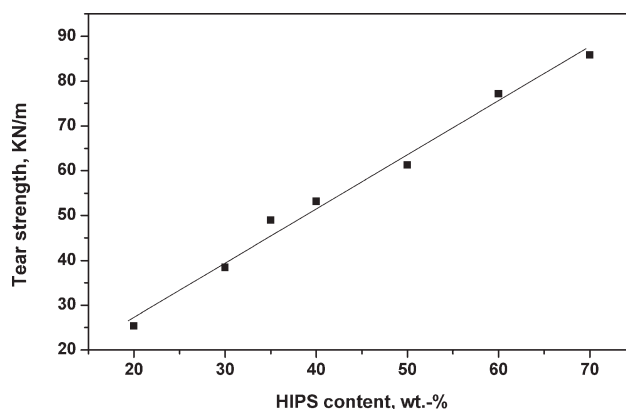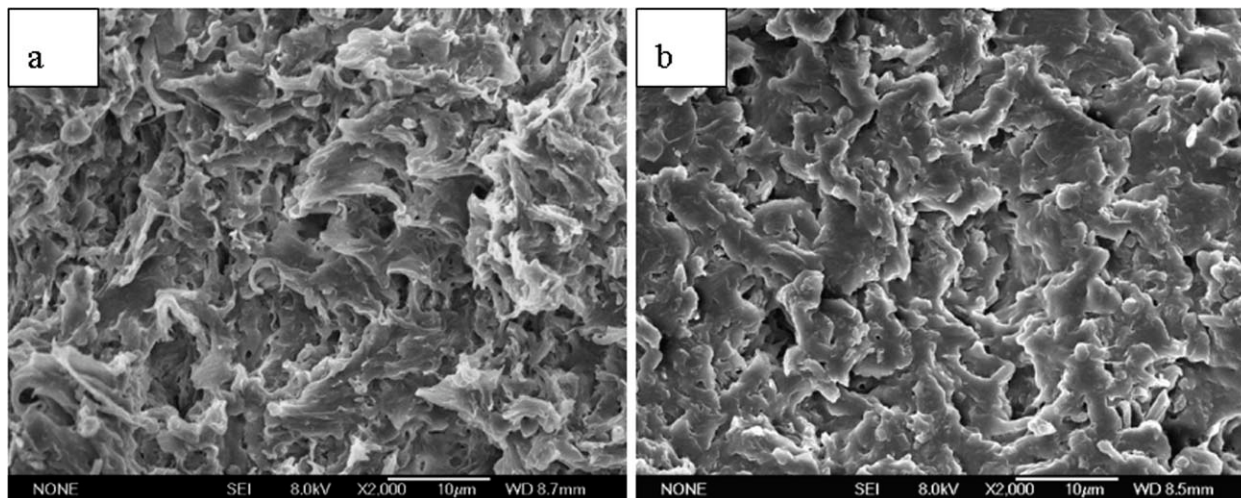
Figure 8 Fracture surfaces of HIPS/SBR blends prepared by the dynamic vulcanization. Blend compositions are (a) 70/30, (b) 40/60 by weight.

particles. The irregular shape of the crosslinked rubber particles shown in Figure 9 indicates that they were produced by break-up of initially large SBR entities under local stress that evolved during melt-mixing. It is noteworthy that the spatial distribution of SBR particles in the TPVs results in the difficulty of flowing through a capillary die for the HIPS/SBR blends melt, leading to high apparent viscosity especially at low shear rate, as shown in Figure 2.

CONCLUSIONS

TPVs based on HIPS/SBR blends were prepared by melt-mixing. Dynamic vulcanization of the blends was performed via conventional sulphur vulcanization systems. The apparent viscosity of the dynamically vulcanized HIPS/SBR blends decreases with the increasing shear rate, indicating the obvious pseudoplastic behavior. At low shear rate, the apparent viscosity of these dynamically vulcanized blends is much higher than that of neat HIPS. The increasing HIPS content in the dynamically vulcanized blends enhances tensile strength and hardness, whereas the elongation at break and tensile set at break reach a maximum at 30 wt % and 50 wt % of HIPS content, respectively. Based on the difference of the stress–strain curves of the dynamically vulcanized blends, we can easily determine that the dynamically vulcanized HIPS/SBR blends can be attributed to TPVs merely only when the HIPS/SBR weight ratio is in the range of 40/60 to 20/80. Finely dispersed SBR phase is found on the etched surfaces of the TPVs using scanning electron microscopy.
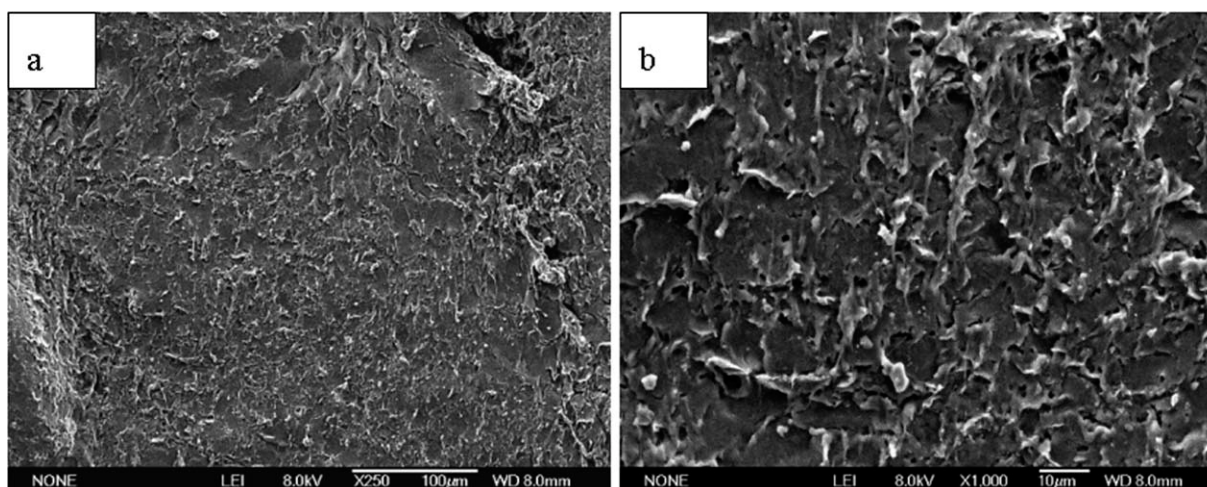

Figure 9 FE-SEM of etched specimens of dynamically vulcanized HIPS/SBR blend with 40/60 weight ratio. (a) at low magnification, (b) at high magnification.

References

1. Chatterjee, K.; Naskar, K. Polym Eng Sci 2008, 48, 1077.
2. Coran, A. Y.; Patel, R. P. In Thermoplastic Elastomers, 2nd ed.; Holden, G., Legge, N. R., Qurik, R. P., Schroeder, H. E., Eds.; Hanser Publishers: New York, 1996.
3. Karger-Kocsis, J. In Polymer Blends and Alloys; Shonaike, G. O., Simon, G. P., Eds.; Marcel Dekker: New York, 1999.
4. Gessler, M. U.S. Pat. 3,037,954 (1962).
5. Fisher, K. U.S. Pat. 3,758,643 (1973).
6. Coran, A. Y.; Patel, R. P. Rubber Chem Technol 1980, 53, 141.
7. Sabet, A.-S. U.S. Pat. 4,311,628 (1982).
8. Duin, M. V.; Machado, A. V. Polym Degrad Stab 2008, 90, 340.
9. Huang, H.; Liu, X.; Ikehara, T.; Nishi, T. J Appl Polym Sci 2003, 90, 824.
10. Goharpey, F.; Katbab, A. A.; Nazockdast, H. J Appl Polym Sci 2001, 81, 2531.
11. Duin, M. V. Macromol Symp 2006, 233, 11.
12. Abdou-Sabet, S.; Puydak, R. C.; Rader, C. P. Rubber Chem Technol 1996, 69, 476.
13. Katbab, A. A.; Nazockdast, H.; Bazgir, S. J Appl Polym Sci 2000, 75, 1127.
14. Nazockdast, H.; Goharpey, F.; Katbab, A. Rubber Chem Technol 2003, 76, 239.
15. Goettler, L. A.; Richwine, J. R.; Wille, F. Rubber Chem Technol 1982, 55, 1448.
16. Han, P. K.; White, J. L. Rubber Chem Technol 1995, 68, 728.
17. Jain, A. K.; Gupta, N. K.; Nagpal, A. K. J Appl Polym Sci 2000, 77, 1488.
18. Jayaraman, K.; Kolli, V. G.; Kang, S. Y.; Kumar, S.; Ellul, M. D. J Appl Polym Sci 2004, 93, 113.
19. Prut, E. V.; Erina, N. A.; Karger-Kocsis, J.; Medintseva, Y. I. J Appl Polym Sci 2008, 109, 1212.
20. Li, Z.; Kontopoulou, M. Polym Eng Sci 2009, 49, 33.
21. Wang, Z. J.; Zhang, X. F.; Zhang, Y.; Zhang, Y. X.; Zhou, W. J Appl Polym Sci 2003, 87, 2057.
22. Zhang, L. Q.; Li, T.; Lu, Y. L.; Tang, Y. W.; Qiao, J. L.; Tian, M. J Appl Polym Sci 2006, 100, 3673.
23. Moly, K. A.; Oommen, Z.; Bhagawan, S. S.; Groeninckx, G.; Thomas, S. J Appl Polym Sci 2002, 86, 3210.
24. Zhang, Z. X.; Zhang, S. L.; Lee, S. H.; Kang, D. J.; Bang C, D. D.; Kim, J. K. Mater Lett 2008, 62, 4396.
25. Manchado, M. A. L.; Arroyo, M.; Kenny, J. Rubber Chem Technol 2001, 74, 211.
26. Prut, E.; Medintseva, T.; Dreva, V. Macromol Symp 2006, 233, 78.
27. Huy, T. A.; Luepke, T.; Radusch, H. J. J Appl Polym Sci 2001, 80, 148.
28. Oderkerk, J.; Schaetzen, G. D.; Goderis, B.; Hellemans, L.; Groeninckx, G. Macromolecules 2002, 35, 6623.
29. Oderkerk, J.; Groeninckx, G. Macromolecules 2002, 35, 3946.