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ORIGINAL PAPER

Influence of ultrafine full-vulcanized powdered rubber on NR/SBR blends

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Abstract In this paper, the use of ultrafine full-vulcanized powdered styrene-butadiene rubber (UFPSBR) in natural rubber/styrene-butadiene rubber was studied. Scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) were employed to characterize UFPSBR. Other testing methods were used to determine the performance of the vulcanizates containing UFPSBR. To analyze the cross-link density of vulcanizates, equilibrium swelling method was used. Dynamic mechanical analysis (DMA) was used to analyze storage modulus (E') and loss tangent (tanδ). SEM results showed that the average diameter of UFPSBR particles was 10 μm approximately. TGA indicated that the amount of inorganic particles in UFPSBR was about 32 % by weight. The testing results of mechanical properties showed that the compounds containing 5 phr UFPSBR had good comprehensive performance. DMA results showed that, according to the values of tanδ, after UFPSBR was added the wet traction performance of the blends was improved.

Keywords UFPSBR · NR/SBR blends · Wet traction · Wear resistance · Dynamic mechanical analysis

Introduction

Traditional polymer blends refers to a compound containing two or three kinds of solid-state polymer materials homogeneously. Natural rubber/styrene-butadiene rubber blend is an essential polymer blend in rubber industry. In this research,

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ultrafine full-vulcanized powdered styrene-butadiene rubber (UFPSBR) was compounded with NR/SBR blends to improve performances of NB/SBR vulcanizates. Dynamic mechanical analysis (DMA) has been widely employed to investigate structure–property correlations and viscoelastic behaviors of polymeric materials [1–4]. The dynamic properties of polymeric materials are of considerable practical significance for several reasons, particularly if they are determined over a wide range of frequency and temperature.

Full-vulcanized can be inferred from its manufacturing process that the surface of rubber particles has higher cross-linking degree than the interior part due to a higher concentration of irradiation sensitives near the surface as well as more reactions with active molecules and ions in water medium. Therefore, the reversible agglomeration of ultrafine full-vulcanized powdered rubber (UFPR) not only has good rubber properties but also can be well dispersed in polymeric materials [5, 6]. To prepare well-distributed UFPR, rubber latex with irradiation sensitives was used as raw material followed by irradiation cross-linking and drying [7]. The chosen rubber latex particles are 50–150 nm in size, the full-vulcanized powdered rubber with size much less than micron scale was called UFPR. Inorganic particles were added to prevent agglomeration of UFPSR.

To characterize UFPSBR, scanning electron microscopy (SEM) was employed to inspect the morphology of UFPSBR. To analyze the amount of inorganic particles in UFPSBR, thermogravimetric analysis (TGA) was employed. Influence of different quantities UFPSBR on various performances of NR/SBR vulcanizates was also investigated.

Experimental

Materials

Natural rubber (NR) used in this study is SCR5 grade, supplied by China Hainan Union Industrial Co., Ltd (Hainan, China). Styrene-butadiene rubber (SBR), SBR-1500 (ML $(1 + 4)100\ ^{\circ}\mathrm{C} = 52$), was purchased from China Jilin Petrochemical Co., Ltd (Jilin, China). UFPSBR, containing a styrene amount of 50 % by weight, is supplied by SINOPEC Beijing Research Institute of Chemical Industry. Other chemical reagents used in the experiment, including sulfur, accelerator *N*-cyclohexyl-2-benzothiazole sulfonamide (CZ), antioxidant 4010NA, zinc oxide, stearic acid, carbon black (N220), and aromatic hydrocarbon oil were all commercial grade.

Equipments and standards

Hitachi 3400 electron microscope (Hitachi, Japan) was employed to conduct SEM. Netzsch STA 449C (Germany) was used for thermal gravity analysis. Hardness of the samples was measured by Shore A type Hardness tester (Yingkou Testing Machine Co., China) according to ASTM D2240. Tensile test was measured by RG L-30A tensile testing machine (Reger, China) according to ASTM D412. Abrasion was measured by GT-7012-A Akron abrasion tester (Gotech, Taiwan) according to National Standard of People's Republic of China GB/T 1689-1998. The cure characteristics, e.g., scorch time (t_{10}), cure time (t_{90}), and torque were determined by GT-M2000-A moving die rheometer (Gotech, Taiwan) at 150 °C according to ASTM D2705. DMA was determined by DMA-2980 dynamic mechanical analyzer (TA Instrument, USA).

Characterization of UFPSBR

In the SEM observation, the USPSBR samples were frozen-dried first and then inspected after being sputter-coated with gold under vacuum condition. For TGA, the temperature range was from 40 to 700 °C, heating rate was 10 °C/min, and the atmosphere for this test was air.

Mastication, compounding, and vulcanization

The details of formulation of each compound are illustrated in Table 1.

The test samples were prepared in the following way: the raw rubber materials were masticated on a two-roll mill for 10 min. Subsequently, other chemical agents were added to the mill and mixed. The temperature of the rolls was kept around 50 °C. Finally, the mixes were vulcanized at 150 °C to their respective cure time (t_{90}) under 10 MPa pressure.

Determination of cross-link density

Cross-link densities of the samples were measured by equilibrium swelling method [8]. Organic additives in the samples were extracted by THF and *n*-hexane, respectively, for 48 h then dried for 48 h at 25 °C. Then the weights of the organic materials-extracted samples were measured. After measured weights, the samples were soaked in *n*-decane for 24 h, and then the weights of the swollen samples were measured. The swelling ratio was calculated according to Eq. (1):

Table 1 Formulations

Title	$1^{\#}$(/phr)	$2^{\#}$(/phr)	$3^{\#}$(/phr)	$4^{\#}$(/phr)	$5^{\#}$(/phr)
NR	70	70	70	70	70
SBR	30	30	30	30	30
UFPSBR	0	2.5	5	7.5	10
Carbon black (N220)	50	50	50	50	50
Accelerator CZ	1	1	1	1	1
Antioxidant 4010NA	2.5	2.5	2.5	2.5	2.5
Stearic acid	2.5	2.5	2.5	2.5	2.5
Zinc oxide	5	5	5	5	5
Sulfur	2	2	2	2	2
Aromatic hydrocarbon oil	6	6	6	6	6

$$Q = 100 \times (W_s - W_u)/W_u \tag{1}$$

where W_s and W_u are weights of the swollen and unswollen samples, respectively. $1/Q$ was used as cross-link density in this experiment. The tests were carried out three times and the results are averaged.

Thermal aging resistance properties

The tensile samples were placed in air circulating oven at 100 °C for 24 h and cooled at room temperature for 12 h, the tensile test was conducted subsequently, according to ASTM D412. The hardness of the samples was tested. The results of these tests were calculated using Eq. (2). Relative properties of tensile properties and hardness were used to evaluate the thermal aging resistance of NR/SBR vulcanizates.

$$\text{Relative properties}(\%) = (P_{\text{aged}} - P_{\text{unaged}})/P_{\text{unaged}} \times 100\% \tag{2}$$

where P_{unaged} and P_{aged} are tensile properties and hardness of unaged and aged samples, respectively.

Dynamic mechanical analysis (DMA)

DMA was carried out in tension mode. The measurements of the samples are 40 × 10 × 2 mm. The frequency of the tests was 10 Hz, the temperature range is from −30 to 90 °C at a rate of 3 °C/min. The storage modulus E', loss modulus E'', and the dynamic loss tangent (tanδ) were calculated by using Eqs. (3) and (4):

$$E'' = E^* \sin\delta \tag{3}$$

$$E' = E^* \cos\delta \tag{4}$$

where E^* is the dynamic complex modulus. The loss tangent was calculated as:

$$\tan\delta = E''/E' \tag{5}$$

Results and discussion

SEM characterization

Figures 1 and 2 show the scanning electron micrographs of UFPSBR at different magnifications. According to Figs. 1 and 2, the diameter of the UFPSBR particles was approximately 10 μm.

Thermogravimetric analysis (TGA)

Figure 3 displayed the mass–temperature curve of UFPSBR from 40 to 700 °C. According to this figure, there was rapid decline of the mass from around 300 to about 500 °C, then the curve had a short plateau region, and then the decline

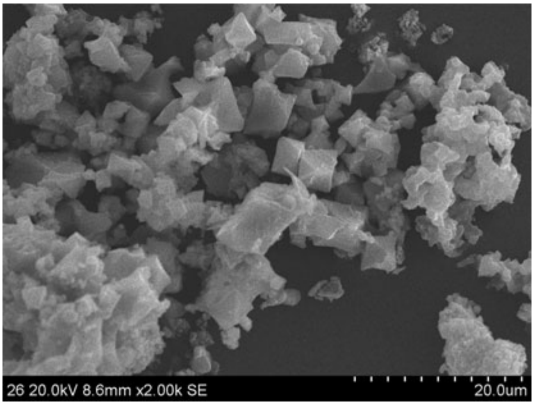

Fig. 1 Scanning electron micrographs of UFPSBR at ×2,000 magnification

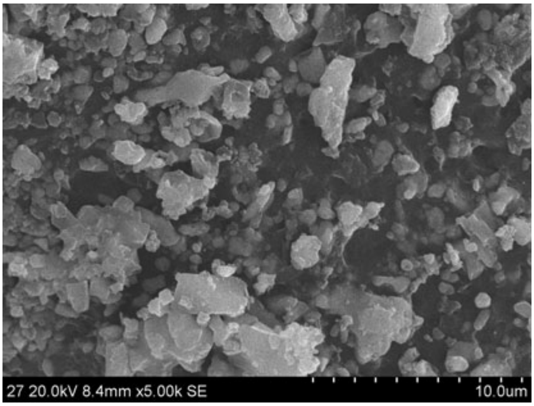

Fig. 2 Scanning electron micrographs of UFPSBR at ×5,000 magnification

reappeared at 600 °C approximately. It can be concluded that at approximate 500 °C, the main component of the sample, i.e., SBR decomposed. The second decline of the sample happened at about 600 °C. The residue of the sample at 700 °C was 32 % by weight approximately. Therefore, the total content of inorganic particles in this type of UFPSBR was about 32 % by weight.

Determination of cross-link density

The results of determination of cross-link density are reported in Table 2. The cross-link density decreases slightly after adding 2.5 phr UFPSBR. The cause of this change was probably due to dispersion of UFPSBR. The presence of UFPSBR provided some additional actively chemical bonds, and these bonds have caused some negative impacts on cross-link density. The cross-link density of other compounds increased by the addition of 5–10 phr UFPSBR; these changes might be because of the presence of UFPSBR containing active chemical bonds made cross-linking easier. The vulcanization reaction between UFPSBR and NR/SBR during the curing progress after UFPSBR was added might be another possible cause to these increases.

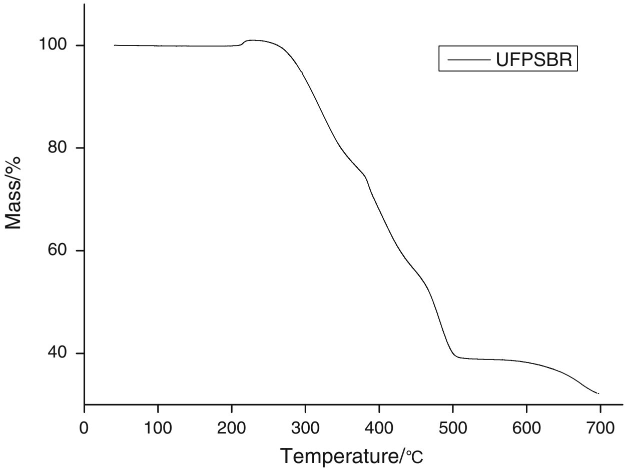

Fig. 3 Mass–temperature curve of UFPSBR from 40 to 700 °C

Table 2 Cross-link density test results of NR/SBR vulcanizates

UFPSBR (phr)	0	2.5	5	7.5	10
1/*Q* (%)	2.07	2.00	2.26	2.53	3.09

Mechanical properties of NR/SBR vulcanizates

The mechanical properties of NR/SBR vulcanizates are presented in Table 3. The NR/SBR blend containing 5 phr UFPSBR exhibits desirable tensile properties. The tensile strength of this blend was 23.7 MPa, comparing to the 20.1 MPa of the blend without powdered rubber, and elongation at break of this blend was 498.9 % comparing to 582.1 % of the pure NR/SBR blend. The increasing of the cross-link density of the NR/SBR vulcanizates was considered as primary reason of these phenomena. In addition, this also may be due to the reaction took place between UFPSBR and NR/SBR during the curing. As 2.5 phr UFPSBR was added, a decrease in tensile strength and an increase in elongation at break are obtained which may be due to the decrease of the cross-link density. When the compound containing 7.5 and 10 phr UFPSBR, respectively, the cross-link densities were higher but the tensile strength was lower. This might be due to the higher cross-link density which damaged the crystalline orientation during the stretching, and took a negative impact on the self-reinforcing of natural rubber. The addition of 2.5–7.5 phr UFPSBR made minor effect on the hardness of NR/SBR vulcanizates. The hardness of NR/SBR vulcanizates increased greatly when 10 phr UFPSBR was added into, possibly due to the higher cross-link density of the samples.

The abrasion test results of the NR/SBR vulcanizates were shown in Table 3. To conclude, the excellent abrasion resistance of NR/SBR vulcanizates was observed when the NR/SBR vulcanizates containing 5 phr UFPSBR, and the abrasion loss

Table 3 The mechanical properties of NR/SBR vulcanizates cured at 150 °C × t_{90}

UFPSBR (phr)	Tensile strength (MPa)	Modulus 300 % (MPa)	Elongation at break (%)	Hardness (Shore A)	Abrasion loss (cm^3/1.61 km)
0	20.1	9.9	498.9	58	0.266
2.5	19.2	8.4	568.9	56	0.280
5	23.7	8.7	582.1	61	0.254
7.5	20.4	9.1	576.7	58	0.304
10	20.0	8.1	566.1	64	0.441
Relative properties (%) (100 °C × 24 h)					
0	−14.9	+34.2	−25.1	+5	–
2.5	−2.8	+32.3	−20.2	+10	–
5	−3.5	+29.4	−9.9	+6	–
7.5	−4.3	+13.9	−5.3	+4	–
10	−3.1	+53.6	−18.8	+5	–

was 0.254 cm^3/1.61 km. When 7.5 and 10 phr UFPSBR were added into the compound, respectively, the cross-link density of NR/SBR blends increased, while the abrasion resistance of these blends decreased. This decrease may be due to the agglomeration of rubber powder in NR/SBR blends which contain higher content of UFPSBR. The agglomeration might engender negative impact on the abrasion resistance of these vulcanizates.

The resistance of the NR/SBR vulcanizates to thermal aging is considered as an essential requirement for long service life of products. The percentage of decrease in mechanical properties as results of aging at 100 °C for 24 h is presented in Table 3. The 300 % modulus of vulcanizates increases considerably after thermal aging due to the increase of cross-link density. The addition of the UFPSBR makes positive effect on the aging resistance of NR/SBR vulcanizates in tensile strength, elongation at break, and hardness; this probably due to a high styrene amount containing in UFPSBR.

Conclusively, the NR/SBR blend with 5 phr UFPSBR showed fine mechanical properties, compared to the NR/SBR blend not containing UFPSBR.

Dynamic mechanical analysis (DMA)

Figure 4 shows the influence of different quantity UFPSBR on dynamic storage modulus (E') and loss tangent ($\tan\delta$), respectively, as a function of temperature for NR/SBR vulcanizates. For the NR/SBR vulcanizates filled with UFPSBR, the curves of storage modulus show the similar trend as that of unfilled sample, in the temperature range of about −30 to 10 °C, as the temperature increased, their storage modulus decline at a faster rate, which indicated that the low-temperature rigidity was more easily affected by the increase of temperature. It is probably due to the increase in rigidity was accompanied by the addition of UFPSBR, the space of chains movement was limited at low temperatures, and additional cross-link density

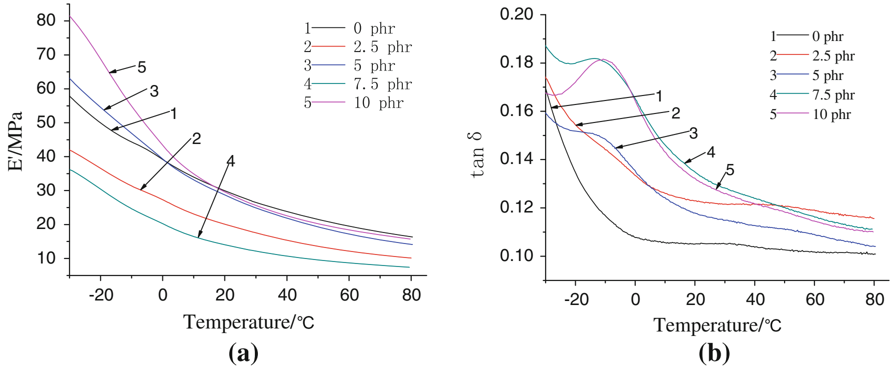

Fig. 4 Dynamic storage modulus (*E*′) (**a**) and Dynamic loss tangent (tan*δ*) (**b**), respectively, as a function of temperatures for NR/SBR vulcanizates filled with different quantity UFPSBR

may also be formed between polymer chains, which showed an increase in storage modulus.

As the temperature increased, the impact of the resistance on them became slightly, the storage modulus closer to those of original unfilled samples. In comparison with unfilled NR/SBR vulcanizates, NR/SBR vulcanizates filled with 2.5 and 7.5 phr UFPSBR show lower *E*′ at the given temperatures. While NR/SBR vulcanizates filled with 5 and 10 phr UFPSBR show higher *E*′ at the given temperatures (about below 0 °C). The tan*δ* values of NR/SBR vulcanizates filled with UFPSBR were all higher than those unfilled NR/SBR vulcanizates when the temperature was above −15 °C, and there was a peak in the vicinity of −10 to 0 °C. As the UFPSBR content increased, the intense and dominant tan*δ* peak becomes more distinct, and the peak value was higher.

It is generally accepted that tan*δ* value determined at 10 Hz and at a temperature fairly far above the T_g of rubbers is a primary data to reveal the energy dissipated per cycle in a rolling tire [9]. The tan*δ* values at 0 and 60 °C reflect the wet traction and the rolling resistance, respectively [10]. A high tan*δ* value at 0 °C indicates a good wet traction property [11, 12], while lower tan*δ* values at 60 °C corresponds to a good rolling resistance after vulcanization.

Therefore, tan*δ* values at 0 °C are used to represent the wet traction, and at 60 °C to demonstrate the rolling resistance. Figure 4 shows the influence of different quantity fillers on dynamic mechanical properties at various temperatures for NR/SBR vulcanizates.

The tan*δ* values of the NR/SBR vulcanizates increased with increase of UFPSBR amount at given temperatures. Especially, tan*δ* value at 0 °C increases higher than that at 60 °C, this could be considered as a constructive trend according to the previous introduction. It indicates that the NR/SBR vulcanizates filled with UFPSBR show good wet traction property, while exhibit low rolling resistance. The tan*δ* values at 0 and 60 °C were 0.108 and 0.102, respectively, for NR/SBR blend not compounded with UFPSBR. For the blend compounded with 5 phr UFPSBR,

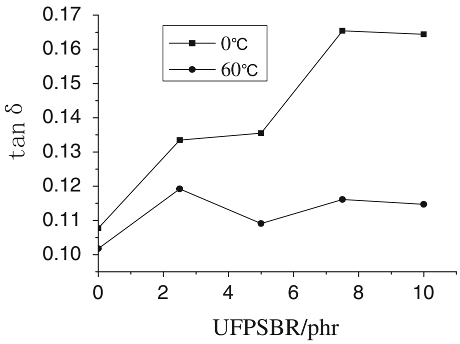

Fig. 5 Dynamic loss tangent (tanδ) as a function of temperatures for NR/SBR vulcanizates filled with UFPSBR

the tanδ values at 0 and 60 °C are 0.136 and 0.109, respectively. Comparing these values with corresponding tanδ values at 0 and 60 °C of NR/SBR blend not compounded with UFPSBR, the tanδ values at 0 °C increased by 25.9 %, and at 60 °C increased by 6.9 %, respectively (Fig. 5).

Conclusion

Scanning electron micrographs indicated that the diameter of the UFPSBR particles was approximate 10 μm. Thermal gravity analysis indicated that the amount of inorganic particles in UFPSBR was about 32 % by weight. The results of equilibrium swelling test indicated that after compounding UFPSBR with NR/SBR compounds, the cross-link density NR/SBR vulcanizates increased. The results of mechanical properties test demonstrated that, the compound contained 5 phr UFPSBR showed good comprehensive performance, comparing with the sample not compounded with UFPSBR. Tensile strength of this compound was 23.7 MPa, increased by 17.9 %; elongation at break was 582.1 %, increased by 16.7 %; and the Akron abrasion loss was 0.254 cm^3/1.61 km, decreased by 4.5 %.

The results of DMA showed that in the range of −10 to 10 °C, the tanδ increased. However, the tanδ value at 60 °C increased slightly. These results indicated that adding UFPSBR into the NR/SBR compound improved the wet traction performance of the blends, although there were some negative impacts on rolling resistance performance. For NR/SBR vulcanizates compounded with 5 phr UFPSBR, the tanδ value at 0 °C increased by 25.9 % and the tanδ value at 60 °C merely increased by 6.9 %, comparing to the blend not compounded UFPSBR. The blends compounded with UFPSBR showed good performance on the wet skid and rolling resistance performance due to its higher tanδ values at 0 °C.

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