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STUDY ON IMPROVEMENT OF ATHLETIC SHOE PERFORMANCE BY ADDING SBS MATERIALS

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Styrene-butadiene-styrene (SBS) block copolymer is a kind of important thermoplastic elastomer (TPE) widely used as sole material of leather shoes, gym shoes, and travel shoes. SBS has become one of the main raw material of sole materials for lots of merits, e.g., low weight density, being comfortable and recyclable, anti-west sides, and no rubber odor and so on. Oiled SBS has worse wear-resisting performance when used as shoe soles. This paper selects the different polymer modifiers and fillers to modify SBS on the base of oiled SBS. The tensile properties, flexibility (degree of hardness) and wear-resisting performance were researched based on athletic shoes. The relations between the modified system's mechanical properties and microstructure were also exposed. Here, we assume that athletic shoes consist of the following materials, e.g., SBS/polystyrene (PS) blend, SBS/Ethylene-vinyl acetate (EVA) blend, SBS/BR blend, as well as SBS/P83 blend. The experiment shows that adding 1 portion of nano-inorganic particles (nano-CaCO3, nano-SiO2) can improve the tensile property and wear resistance of SBS/PS blend; When the ratio of SBS/BR is 90/10, the comprehensive performance of the material is better, and its softness and wear resistance are further improved. When ten P83 was added, the wear resistance and softness of the SBS/P83 blend were improved.

Keywords: SBS; blending; nano-composites; flexibility; wear-resisting performance; athletic shoes

1. Introduction

Thermoplastic elastomer is a major breakthrough in the application of polymer science and engineering. It has both the characteristics of rubber and thermoplastics: it shows high elasticity of rubber at normal temperature, and can be plasticized at high temperatures. It is the so-called "third-generation rubber" after natural rubber and synthetic rubber, or “thermoplastic rubber”, or TPR for short [1-2].

At present, the main type of thermoplastic elastomer (TPE) is styrene-butadiene-styrene triblock copolymer (SBS), which accounts for more than 70% of TPE. SBS has both plasticity and rubber resilience [l]. It can be in contact with water, weak acids, alkalis, etc. It has excellent tensile strength, large surface friction coefficient, good low-temperature performance, excellent electrical

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properties, and good processing properties. As an important thermoplastic elastomer, SBS is widely used as the sole material in the production of medium and high-end leather shoes and travel shoes [3-6]. Being light, comfortable, anti-slip, recyclable and having no rubber odor, it has become one of the most important raw materials for making athletic shoes soles [7]. Generally speaking, a large amount of softening oil needs to be added to SBS to improve its fluidity and softness. However, the wear resistance of the oil-filled SBS is greatly reduced [8]. Although currently it is difficult or even impossible to have an elastomer having excellent comprehensive properties with both abrasion resistance and softness, a large amount of ordinary inorganic particles are often used in production to the oil-filled SBS matrix to improve wear resistance and reduce costs.

At present, the research on the modification of SBS sole materials mainly focuses on adding a single modifying component to SBS and investigating the change laws of mechanical properties of the modified system. It is reported that transparent polystyrene (PS) has the advantages of easy molding, small shrinkage, low hygroscopicity, and good thermal properties; butadiene rubber (BR) has excellent softness and wears resistance [9]. Ethylene-vinyl acetate copolymer (EVA) has high strength and good softness [10]. Powdered nitrile -butadiene rubber (NBR) has good abrasion resistance, soft resistance, and oil resistance [11]. Inorganic particles have advantages in improving mechanical strength, wear resistance, and inexpensive[12]. The abrasion-resistant, soft polymer and nano-inorganic particles are used in combination with modified oil-filled SBS to take advantage of their respective performance in order to obtain an elastomeric material with excellent comprehensive properties that have both abrasion resistance and softness [13-15].

Therefore, this article focuses on improving the tensile and abrasion resistance of oil-filled SBS materials (reflected by abrasion), and maintaining or improving the softness of the material (reflected indirectly by hardness). It studies the use of PS and its modification with SBS in combination with inorganic particles ($CaCO_3$, nano-$CaCO_3$, SiO_2, nano-SiO_2), exploring the masterbatch method for tensile strength, elongation at break, elongation at break, and permanent deformation at the break of SBS, softness (hardness) and abrasion resistance. It also investigates the relationship between the macroscopic properties and the micro-structure of the modified materials through analyzing the SEM photographs of the nano-inorganic particles dispersion of the worn surface. On the basis above, further investigation was made to discover the flexibility of BR, P83 and their use with nano-$CaCO_3$ and nano-SiO2 in terms of hardness and abrasion resistance. This study aims to find a sole material with excellent comprehensive properties that has both flexibility and wear resistance.

2. Experiments Equipment and Materials

2.1 Main materials and instruments

The main raw material of the experimental mainly is SBS tri-block thermoplastic elastomer: No. F475B, First-grade product, Maoming Petrochemical. The location of athletic shoe consisting of SBS is seen from Figure 1. Apart from the raw materials, we also adopt the following materials.

Transparent polystyrene (PS): Grade PG-33, main properties: tensile strength≥46.0MPa, Rockwell hardness 77;

Ethylene-vinyl acetate copolymer resin (EVA resin): brand E180F, VA content 18%, main properties: tensile strength ≥ 29.0MPa, elongation at break ≥ 800%, Shore A hardness 38;

Butadiene rubber (BR): Grade BR9000, first-class product, main properties: tensile strength ≥13.7MPa, elongation at break ≥430%;

Powdered nitrile rubber (NBR): grade P83, AN content 33%;

Nano calcium carbonate (nano-CaCO3): industrial grade, treated with 2% titanite (mass parts);

Active micro calcium carbonate (CaCO3): grade Pd-40, average particle size 1um;

Ultrafine white carbon black (nano-SiO2): industrial grade, treated with 2% silane coupling agent (mass parts);

White carbon black (SiO2): industrial grade, with an average particle size of 10um, treated with 2% silane coupling agent (mass parts);

Other reagents used in the experiment: antioxidant 264, antioxidant 168, stearic acid (HST).

2.2 Experimental instruments and testing analysis

The SBS samples used in the experiment were from maoming petrochemical, which needed the experimental instruments: Electronic universal testing machine (CMT-6104), Shenzhen new think twice measurement technology co. LTD; Abrasion testing machine (WML-76) Jiangsu jiangdu zhenwei testing machinery co. LTD; Shore A hardness tester (LX-A), Shanghai liuling instrument factory.

2.2.1 Tensile performance test

The CMT-6104 electronic universal testing machine was used to test the tensile strength, elongation at break, fixed tensile strength and permanent deformation of the sample according to GB/T528-92, and the tensile speed was 500±50mm.min^{-1}. ①Mark the working section on the prepared dumbbell shaped specimen and number it on both ends. Measure the thickness of the sample within the standard distance with a thickness gauge, measure three points, and calculate the average value as the thickness value of the working part. Measure the length of the working part with a vernier caliper. ②Set up the experimental procedure, including: the stretching speed is 500±50)mm/min;The physical parameters to be measured in the experiment include tensile strength s, 100% and 300% constant tensile strength S, elongation at break e and other parameters. ③Start the motor to stretch the sample until it is broken, and read the result from the computer; ④Measure the length (scalar segment) of the sample after fracture after 5min, and calculate the permanent deformation of the tear.

2.2.2 Hardness testing

According to GB531-76 to test the hardness of TPE, this paper adopts LX-A shao rubber hardness tester.①Put the sample on a firm plane, hold the durometer, press the pin in the middle hole of the foot at least 12mm away from the edge of the test block, press the foot on the sample steadily, without any vibration; ②Keep the pressing foot parallel to the surface of the sample, so that the pressing needle can be pressed vertically into the sample;③Measure the hardness value at different positions at least 6mm apart for 5 times, and take the average value as the final result.

2.2.3 Wear resistance test

The abrasion of elastomer was measured by akron abrasion tester (GB 1689-1998).The diameter of the rubber wheel used for the test is 68mm, the thickness is 12.7±0.2 mm, and the hardness is 75 ~ 80 (Schor type A). The central aperture should conform to the diameter of the rubber wheel shaft. The rotation speed of the rotary shaft of the rubber wheel is 76r/rad, and the rotation speed of the grinding wheel is (33~35) r/min. Experimental principle: under the load of 27.6n, the sample on the rubber wheel contacts with the grinding wheel at a certain inclination Angle (generally, 150° is selected) to generate wear due to rolling friction. The wear volume of the sample within the 1.61km range is measured (600rad is prepolished first, then 3416rad is polished).

2.3 Sample preparation

2.3.1 Mixing

Common blending method: control the temperature of the front roller at 125~125℃, and the temperature of the back roller at 120~125℃. Mix all ingredients with SBS in a certain proportion, strictly control the roll distance and mixing times, and mix 8~10min to produce tablets.0

Master material method: the temperature of the front roller was controlled at 125~125℃, and the temperature of the back roller was 120~125℃. A part of SBS was mixed with the nanometer filler to form the master material, and the other components were added after mixing for 3-5min. The roll spacing and mixing times were strictly controlled, and the sheet was produced after mixing for 5-6min.

Fig. 1 Athletic shoe consisting of SBS

2.3.2 Linking piece

Pressing process: weigh and take the sample, adjust the temperature of the vulcanizing machine to 160~165℃, preheat for 2-3min, then press for 3min (pressure 8~10MPa), and finally press for 2min (pressure 6 ~ 8MPa), then take out the sample number. In addition, Table 2 describes the necessary equipments in the experimental part.

3. Experimental Results and Discussion

Our experiments consist of four parts:(1) Stress-strain of oil-filled SBS; (2) PS and its modification with SBS in combination with inorganic particles; (3) EVA and its modification of SBS with nano-inorganic particles; and (4) Wear-resistant and soft components and modification of SBS with nano-inorganic particles.

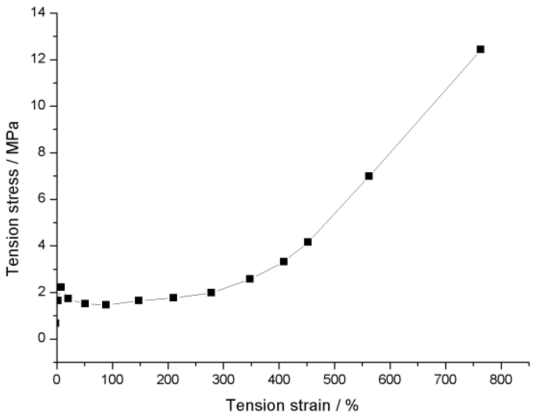

Fig. 2. Stress-strain of oil-filled SBS

3.1 The evaluations of stress-strain of oil-filled SBS

Thermoplastic elastomer SBS has better tensile strength, tear strength and elongation at break. Tensile performance tests show that the material behaves like plastic at room temperature. At first, it is similar to the cold-drawing phenomenon of general plastics. At the strain of about 10%, necking occurs and the stress suddenly drops. Subsequently, as the narrow neck gradually developed, the stress was almost constant, and the strain continued to increase until the development of the narrow neck was completed, at which time the strain was about 300%, as seen from Fig. 2. When the SBS is further stretched, the fine neck is uniformly stretched, and the stress is further increased, which can reach 15.20Mpa. At the same time, the maximum strain can reach 893.8% or even higher. In the process of continuous stretching, according to the "stress-induced plastic-rubber transition' theory, the plastic phase in the sample was completely shredded into fine regions and dispersed in the rubber phase. The rubber phase became the only continuous phase and the material showed high elasticity. This causes a second turning point in the curve, and the stress increases with strain up to the breaking point. The two turning points on the tensile curve are related to the sudden appearance of the narrow neck and the subsequent destruction of the continuous phase of the plastic into microscopic regions dispersed in the continuous phase of the rubber.

3.2 PS and its modification with SBS

As one of the six general-purpose plastics, PS is an amorphous linear polymer, which is known for its excellent dielectric and electrical insulation properties. Fig. 3 shows the effect of PS on tensile strength and elongation at break of SBS. It can be seen that as the PS content increases, the tensile strength of the material gradually increases. When the amount of PS added reached 15 parts, the tensile strength reached a maximum of 17.13 MPa. But as the PS continued to increase, and the tensile strength of the material gradually decreased. When the PS is added in an amount of 35 parts, the tensile strength of the material is reduced to 16.46MPa. But compared to oil-filled SBS, the tensile strength is still improved. The elongation at break is not significantly reduced when the PS content is low. When the PS content reaches 15 parts, it only decreases by 22.8%, but when the PS content exceeds 15 parts, the elongation at break becomes larger.

Fig. 4 shows the effect of PS on the tensile strength of SBS. It can be seen that as the PS content increases, the elongation strength gradually increases. When 15 parts of PS are added, the 300% elongation strength reaches 3.57MPa and the 100% elongation strength reaches 1.66MPa. At this time, the material behaves as a typical Rubber tensile behavior, that is, greater deformation under less tensile stress. As the PS content continues to increase, the tensile behavior of the system gradually changes to that of the hard elastomer. When the PS content reaches 35 parts, the 300% elongation strength becomes 7.58 MPa and the 100% elongation strength becomes 3.14. MPa.

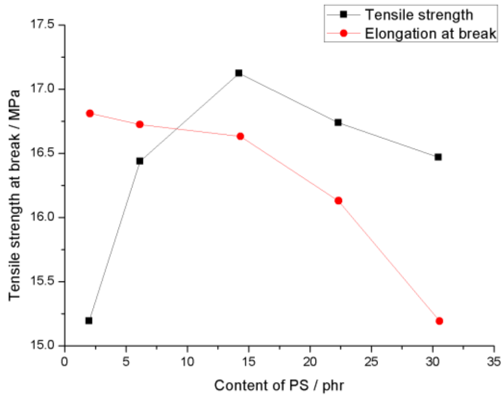

Fig. 3. Effect of PS on SBS in mechanics

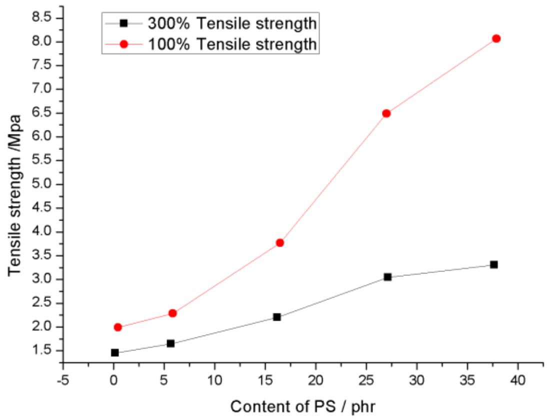

Fig. 4. Effect of PS on SBS in stretching strength

Fig. 5 shows the effect of PS content changes on the permanent deformation of SBS. It can be seen that the breaking permanent deformation of pure oil-filled SBS is small, only 20%. When the PS content is small, the increase in the permanent breaking deformation of the blend is not obvious. When the PS content reaches 15 parts, the permanent breaking deformation of the blend increases to 48%.

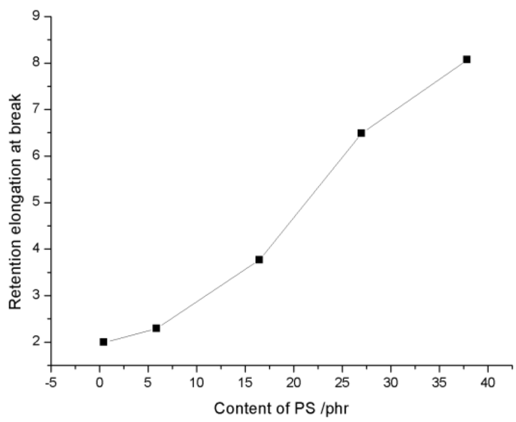

Fig. 5. Effect of PS on SBS in shape change

After that, as the PS content increased, the permanent deformation of the material increased significantly. When 35 parts of PS were added, the permanent deformation at break reached 142.5%. At this time, the blend showed PS stretching characteristics, and the resilience of the material was significantly deteriorated.

3.3 EVA and its modification of SBS with nano-inorganic particles

From the results of PS studied in the previous section, it can be seen that PS can improve the tensile strength and abrasion resistance of SBS, but reduces its softness. Another elastomer EVA was introduced to modify SBS, and it is hoped to solve this problem.

EVA is a random copolymer of ethylene-vinyl acetate. It has a tacky feel (but no glue on the surface), is white and transparent. It has large softness and adhesion, excellent impact resistance, environmental stress crack resistance, and ultraviolet light resistance. EVA is an important elastomer material for shoes. SBS and EVA have their own advantages and disadvantages when applied to soles. Therefore, it is expected that they will be melt-blended to obtain excellent performance.

For the SBS/EVA binary blending system, compatibility is an important factor in examining how well EVA can modify SBS. According to the most commonly used solubility similarity principle for predicting the compatibility of polymers, EVA is a weakly polar polymer material (its solubility parameter d is 17.75J12/cm32), and it is compatible with SBS (the solubility parameter d is 18.1 ~ 18.5J12/cm32).

Fig. 6 shows the effect of EVA on tensile strength and elongation at break of SBS. It can be seen that with the addition of EVA, the tensile strength of the material gradually increases. When the EVA reaches 15 parts, its tensile strength reaches a maximum value of 17.07 MPa. When the EVA continues to increase, the tensile strength of the material gradually decreases. The elongation at break is not obvious when the EVA content is low. When the EVA content reaches 15 parts, the elongation at break is 882.6%, which is only 11.2% lower than that of oil-filled SBS, but when the EVA content exceeds 15 parts, the drop in elongation at break becomes larger.

Fig. 7 is the change curve of the tensile strength of the SBS / EVA blend when EVA is added to SBS. It can be seen that as the EVA content increases, the elongation strength gradually increases. When the amount of EVA is 15 parts, the 300% elongation strength increases from 1.88MPa to 2.35MPa, and the 100% elongation strength increases from 1.38MPa to 1.67MPa. As the EVA content increases, its elongation strength continues to increase. When the amount of EVA is 75 parts, the 300% elongation strength increases to 4.21MPa, and the 100% elongation strength increases to 3.42 MPa. Compared with the addition of PS, the rubber characteristics are more obvious when stretched.

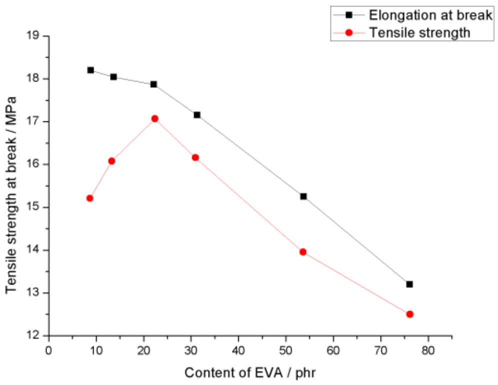

Fig. 6 Effect of EVA on SBS in dynamics

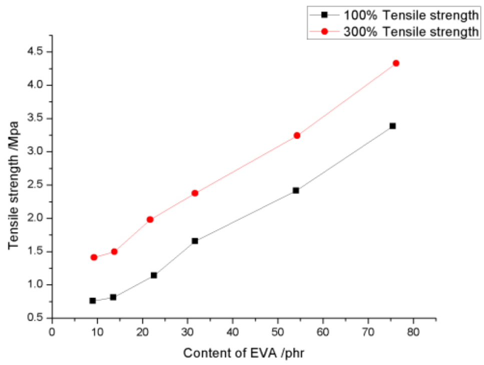

Fig. 7 Effect of EVA on SBS in stretching strength

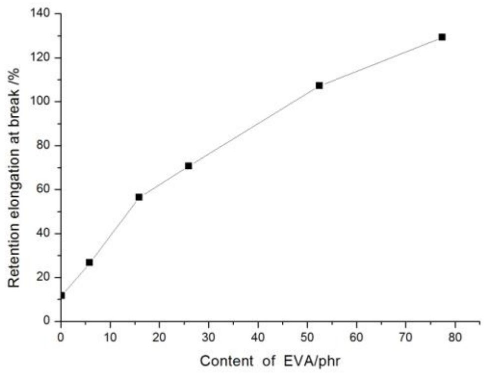

Fig. 8 Effect of EVA on SBS in the permanent set at break

When EVA is added, the breaking permanent deformation of the SBS/EVA blend has the same trend as that of SBS/PS, and the breaking permanent deformation gradually increases with the increase of the amount added shown in Fig. 8. With 15 parts of EVA, the permanent deformation at break is increased from 20% to 60%, and at 75 parts of EVA, the permanent deformation at break is increased to 127.5%. At this time, the resilience of the material is significantly worse.3.4 Wear-resistant and soft components

The previous research shows that after adding PS, although the tensile strength, wear resistance of elastomer materials and permanent deformation of the material have been greatly improved, the softness of the material is reduced. The tensile strength of modified materials is higher than that of SBS, and the flexibility is also increased, but the wear resistance is reduced. For this reason, it is hoped to find a component that is both abrasion-resistant and soft, and to modify SBS with nano-inorganic particles, to obtain a modified material with excellent comprehensive properties that have both softness and abrasion resistance.

Fig. 9 shows the effect of BR on the tensile strength of SBS/PS/ nano-$CaCO_3$ blends. It can be seen from the figure that after adding BR to the elastomer material, its tensile strength has been decreasing. When 5 parts of BR is added, the tensile strength of the material is reduced to 16.68 MPa; when the BR content reaches 10 parts, its tensile strength is reduced to 15.66 MPa. It can be seen that BR reduces the tensile strength of the elastomer material. The elongation at break is inconsistent with the change in tensile strength. When 5 parts of BR is added, the elongation at break reaches a maximum of 869.2%. When the amount of BR added exceeds 5 parts, the elongation at break of the elastomer material gradually decreases. When 10 parts of BR are added, the elongation at break decreases to 841.2%, and the decrease increases after more than 10 parts. This shows that a small amount of BR can increase the elongation at break of the material, but when too much BR is added, the compatibility between BR and SBS becomes poor and the elongation at break of the material decreases.

Fig. 10 shows the effect of BR change on the permanent deformation of SBS/PS/nano-$CaCO_3$. It can be seen that when 10 parts of BR are added, the breaking permanent deformation is reduced from 51.4% to 43.8%, and when the amount of BR is added to 20 parts, the breaking permanent deformation is reduced to 32.5%. It can be seen that the addition of BR reduces the permanent deformation of the elastomeric material and increases resilience. Fig. 11 shows the relationship between the BR content and the hardness of the SBS/PS/nano-$CaCO_3$ blend. It can be seen that the hardness decreases sharply after adding BR, and the hardness decreases more with the increase of BR. When the amount of BR added is 10 parts, the hardness drops to 68. At this time, its softness is much better than that of oil-filled SBS.

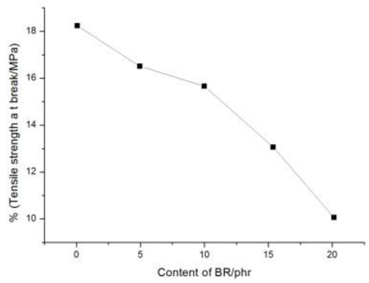

Fig. 9 Effect of BR on the mechanical properties of SBS/PS/nano-$CaCO_3$ ternary blends

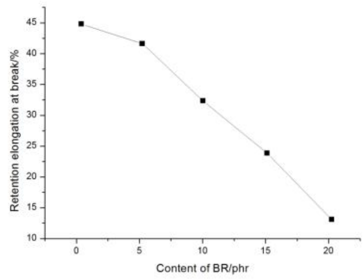

Fig. 10 Effect of BR on the retention elongation at break of SBS/PS/nano-CaCOz ternary blends

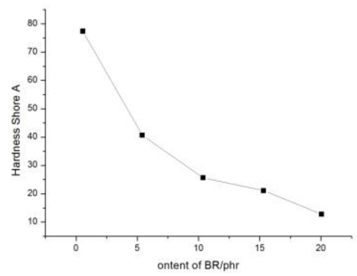

Fig. 11 Effect of BR on the hardness of SBS/PS/nano-$CaCO_3$ ternary blends

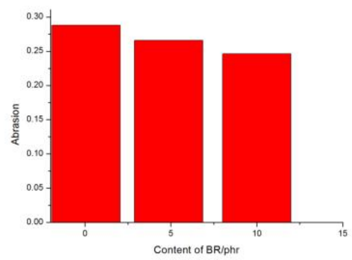

Fig. 12 Effect of BR on the abrasion of SBS/PS/nano-$CaCO_3$ ternary blend

Therefore, only 5 and 10 parts of BR are added here. It can be seen from Fig. 12 that the abrasion of BR is decreasing as the content of BR increase, and the abrasion decreases to $0.2256cm^2/1.61k$ when adding 10 parts of BR , which proofs that and the wear resistance of the material is improved at this time. BR is a general-purpose rubber with excellent abrasion resistance. It has good compatibility with SBS. After blending with SBS, it blends into the SBS soft phase to form a BR 'microsphere". This "microsphere" strengthens the SBS-PB soft phase, enhance the anti-wear and anti-friction effect of SBS, and improve the wear resistance of elastomer materials.

Fig. 13 shows the effect of P83 on the tensile strength and elongation at break of SBS. It can be seen that after adding P83, the tensile strength of the material shows a downward trend. When 5 parts of P83 is added, the tensile strength of the elastomer material decreases to 14.01MPa, and when the content of P83 is 10 parts, the tensile strength of the material decreases to 13.41MPa. The elongation at break of the material also continued to decrease as the content of P83 increased. When 5 parts of P83 was added, the elongation at break was reduced to 870.6%, and when 10 parts of P83 was added, the elongation at break was reduced to 852.9 %. It can be seen that P83 has an adverse effect on the tensile properties of the elastomer.

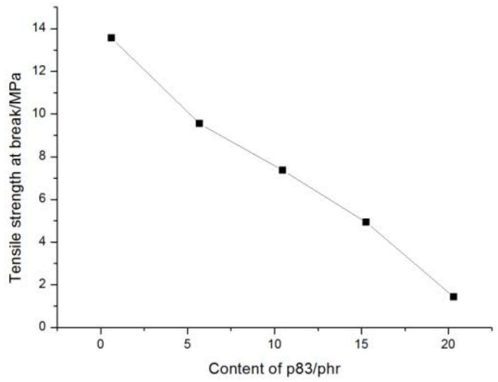

Fig. 13 Effect of P83 on the mechanical properties of SBS

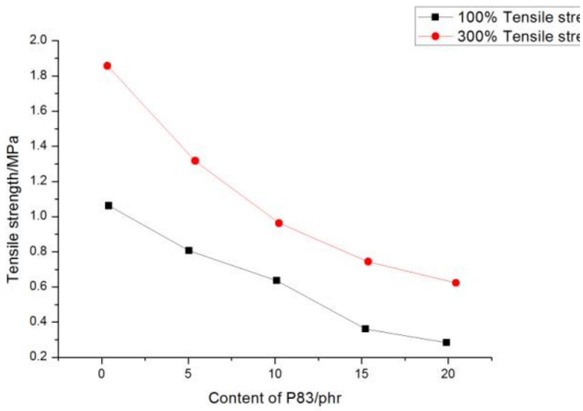

Fig. 14 Effect of P83 on the tensile strength at break of SBS

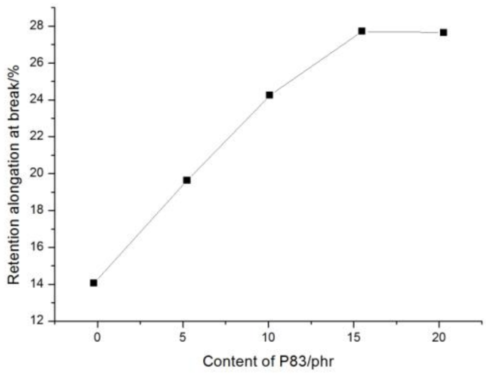

Fig. 15 Effect of P83 on the retention elongation at break of SBS

Figs. 14 and 15 show the effect of P83 on the tensile strength and permanent deformation of SBS. It can be seen that with the increase of P83, the tensile strength of the material shows a downward trend (this is different from the performance of PS and EVA). When 5 parts of P83 is added, the 300% tensile strength is reduced from 1.88 MPa to 1.54 MPa, and the 100% fixed The tensile strength decreased from 1.38MPa to 1.22MPa; when 20 parts of P83 were added, the 300% fixed tensile strength decreased to 1.09MPa, and the 100% fixed tensile strength decreased to 0.86MPa. At this time, the softness of the elastomer material is much lower than the level of pure SBS, which is the typical tensile behavior of rubber. With the addition of P83, the permanent deformation of the elastomeric material has increased, but the increase is small. When 10 parts of P83 are added, the permanent deformation of the fracture is only increased by 8.5%, which is higher than that of the same amount of PS and EVA. Resilience is better.

4. Conclusion

The effects of PS and its combination with inorganic particles ($CaCO_3$, nano-$CaCO_3$, SiO_2, nano-SiO_2) on the tensile strength, elongation, softness (hardness) and wear resistance were investigated.The results showed that when 15 PS were added, the tensile properties of SBS/PS blends were the best, the wear resistance was improved, and the softness was not significantly reduced.The addition of ordinary inorganic particles ($CaCO_3$, SiO_2) reduced the tensile properties and softness of SBS/PS blends.The tensile properties and wear resistance of SBS/PS blends can be improved by adding 1 part of nano-$CaCO_3$ and nano-SiO_2.The properties of SBS/PS/nano-$CaCO_3$ ternary elastomer materials can be further improved by the master material method. On the other hand, the application of EVA with nano-$CaCO_3$ and nano-SiO_2 and the effect of master material method on SBS mechanical properties were investigated.The results showed that when 15 EVA were added, the tensile strength and softness of SBS/EVA blends increased, but the wear resistance decreased.Adding 1 part of nano-$CaCO_3$ and nano-SiO_2 can improve the tensile strength and wear resistance of SBS/EVA blends.The influence of BR, P83 and nano-$CaCO_3$ on SBS mechanical component energy was investigated. SEM was used to observe the influence of the dispersion of nano-inorganic particles on the properties of elastomer materials and the influence of various modifiers on the wear resistance of elastomer materials.The results showed that: when the ratio of SBS/BR was 90/10, the comprehensive performance of the material was better, and its softness and wear resistance were further improved.The wear resistance and softness of SBS/P83 blends were improved when 10 copies of P83 were added.The Athletic shoe consisting of SBS have good softness and wear resistance.

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