Modification of MMT by different modifiers and their effects on the mechanical properties of SBS

XiuhuaYu[1], GuojunCheng[1*], MuqingSi[1], GuoxinDing[1], ZhoufengWang[1], KonghuTian[1], Chuyang Xu[1]

[1]*School of Materials Science and Engineering, Anhui University of Science and Technology, Huainan 232001, China*
Corresponding author: GuojunCheng
E-mail:chengguojun0436@126.com

Abstract: In order to improve the surface activity of montmorillonite (MMT) and its compatibility with polymers,three modifiers of(3-aminopropyl)triethoxysilane(KH550), 2,3-epoxypropoxy propyltrimethoxysilicane (KH560) and 3-methacryloxypropyltrimethoxysilane (KH570) were chosen and used for the modification of MMT with different dosages through wet processing.The structure ofmodified MMT was characterized by infrared spectrum (IR), X-ray diffraction (XRD)and contact angle tester, and themodification mechanism by different modifiers was taken simultaneously. Theresults showed that three modifiers have achieved the desired effect on the surface modification of MMT, and the contactangles all increased more than 20° at optimum concentration. The MMT/thermoplastic styrene-butadiene rubber (SBS) nanocomposites were prepared by double roll smelting techniqueaccording to the experimental formula. Compared with unmodified MMT, the comprehensivemechanical properties of SBS has been significantly improved by theMMT after modification. When less than 3% of modified MMT was added, the melt flow properties, wear resistance and solvent resistance of SBS were also obtained considerableperfection. Among them, the modification effect of KH570was dominant.

Keywords: modifier, montmorillonite, modification, SBS, property.

Introduction

Montmorillonite (MMT) is a kind of nano-silicate clay. Because of its wide source, low price, unique layered structure and excellent mechanical properties, and it has now become one of the important inorganic raw materials of high performance polymer/ clay nanocomposites[1].

Many unique crystalline chemical properties of MMT are derived from its unique lattice structure. These properties include cation exchange, swelling, adsorption, water absorption, dispersibility and lubricity. While the microenvironment between MMT sheets is relatively hydrophilic, the polymers and organic monomers are relatively hydrophobic. Therefore, the microenvironment between MMT sheets is not conducive for the insertion

of polymers and organic monomers[2-3]. In order to solve this problem, the surface modification of MMT has become an indispensable part in the process of preparing nanocomposite materials. The main principle of surface modification is the reaction of amphiphilic molecules with MMT, so that the inorganic end adheres to the silicate sheet, and the organic end remains between the layers and the surface, thereby improving the microenvironment between the layers[4-6].

Thermoplastic styrene butadiene rubber (SBS) is a triblockcopolymer made from living anionic polymerization initiated by styrene and butadiene as monomers and alkyl lithium as the initiator[7]. Inexpensive and widely used, SBS has unique applications in plastic modification, shoe industry, waterproof coating, asphalt modification, sealing materials, and also in adhesives, wires, auto parts, cables, medical equipment parts, household appliances. One of the most hot research fields of SBS is the modification of asphalt. Adding an appropriate amount of SBS and inorganic powder materials to asphalt can significantly improve the anti-ultraviolet aging resistance, rheology and elastic recovery of asphalt[8-10].As the thermoplastic elastomer with largest productivity, the industry of SBS has matured through long-term development. However, as the performance requirements of materials in production become higher and higher, modified SBS still has huge potential development prospects[11-12].

Nanomaterial is a general term for solid materials with an average particle size in the nanometer range (1~100nm). Composites with at least one phase whose size is smaller than 100 nm are called nanocomposites. Many substances can be used as one of the phases of nanocomposite materials, such as metal, ceramic or polymer. Nanomaterials have the characteristics of smaller average particle size, larger specific surface area, more surface atoms, and higher surface free energy. Therefore, they exhibitunique characteristics such as small size effects and surface effects. The monomer or polymer can be inserted between the layers of the clay sheet by a certain method, so that the clay sheet layer is peeled off and uniformly dispersed in the polymer matrix. In this way, polymer/clay nanocompositesthat the layered clay and the polymer are compounded on a nanometer scalecan be prepared[13-14].

Because of the large interface between the matrix and the dispersed phase, the properties of the matrix and the dispersed phase can be fully combined. Therefore, compared with the matrix material, the performance of the nanocomposites is greatly improved in all aspects. Compared with conventional polymer-based composites, themechanicsperformance, dimensional stability and thermal stability of polymer/clay nanocompositescan be greatly improved with only a few fillers (mass fraction <5%). The clay is oriented in a plane in the polymer/clay nanocomposite, as a result, the polymer/clay nanocomposite film possess a high barrier property[15-16].

In the present work,(3-aminopropyl)triethoxysilane (KH550), 2,3-epoxypropoxy propyltrimethoxysilicane (KH560) and 3-methacryloxypropyltrimethoxysilane (KH570) were investigated as modifiers for MMT/SBS nanocomposites. On the one hand, the side groups on the main chain of modifiers may react with -OH, -NH and -NH$_2$ on the surface of the MMT containing active hydrogen, and modifiers containcarbon chain

structure and can provide great compatibility with organic polymer. On the other hand, the interfacial modification was realized via a simple melt compounding. Various characterizations were used to reveal modifiers's influence on the microstructure of the nanocomposites and the results were correlated to their final performance.

2. Experiment

2.1 Materials

MMT used for this study wasindustrial grade and from Hongli Plastic Materials Co., Ltd., Shenzhen, China. Modifiers of KH550, KH560 and KH570 was purchased from Nanjing Shuguang silane Chemical Co., Ltd., Nanjing, China.Thermoplastic styrene-butadiene rubber (SBS), with trademark 4452, was manufactured by Sinopec Beijing Yanshan Petrochemical Branch, Beijing, China. Other rubber additives were industrial grade and used as received.

2.2 Preparation of modified MMT using modifiers

Before modification,neatMMTwas dried at 110 °C in a vacuum oven for 10 h to remove adsorbed moisture from the surface. Alcohol aqueous solution was prepared with absolute ethanol and deionized water at a volume ratio of 9: 1, then an appropriate amount of glacial acetic acid was added to adjust the pH = 4. A certain amount of the coupling agent was weighed and dissolved in an alcohol aqueous solution, then the obtained solution wasreplaced into a reaction kettle to hydrolysis at 60! for 1 h. At the same time, Quantitative MMT was dissolved in an alcohol solution for ultrasonic activation for 40 min. After the activation was completed, it was replaced into the reaction kettle previously mentioned then heated at 75! for 2 hours. After the reaction was completed, the mixture was suction-filtered, washed successively with deionized water and absolute ethanol, thenfiltered. The obtained product was then placed in an electric heating constant temperature air drying oven for 24 hours.MMT before and after modificationwas coded as MMT-550, MMT-560 and MMT-570to ease the following discussion.

2.3 Preparation of MMT/ SBS nanocomposites

SBS, MMT and additives were mixed with a double roll millatthe beginning temperature of 110 °C. The compounds were then compression molded into 2 mm thickness sheets by 140 °C.

2.4 Characterization

Infrared spectroscopy (IR), X-ray diffraction (XRD)and contact angle measuring instrument (CAMI) were performed to characterize the structures and surface properties of MMT before and after surface modification.IR spectrawere collected on a VERTEX 80+HYPERION 2000 spectrophotometer (Bruker Optics, USA) with a resolution of 4 cm-1 for which the samples were palletized with KBr powder.The crystalline structures of the MMT before and after modification were examined via XRD analysis using a

Smartlab SE (Japan's neo-confucianism Cu target, Kα radiation, λ = 1.54178 Å) at 40 kV and 40mA in the 2è range of 5-60 ° at room temperature.The contact angle was investigated using CAMI (SL 200C, USA) at 25 °C. The surface of the sample was dropped by water and the angle value was taken as its contact angle.

The tensile tests ofMMT/SBR/nanocomposites were performed following ISO standard 37: 2005. Tensile strength, stress at 100% and elongation at break were measured using a WDW-50 instrument. Shore A hardness was measured according to ISO standard 868: 2003.

3. Resultsand Discussion

3.1 Structural characterization

The infrared spectrum of MMTmodified by KH550, KH560, KH570 and the raw material were shown in Figure 1 (A), (B), and (C), respectively. In the infrared spectrum of sodium-based MMT, thevibration peak of hydroxyl groups on the surface of MMTwas at 3625 cm^{-1}.The peaks of stretching vibrations and bending vibrations of hydroxyl groups of adsorbed water between the layers were at 3442 cm^{-1} and 1635 cm^{-1}, respectively. The peak at 1039 cm^{-1}indicated the stretching vibration of the Si-O-Si bond while the peak at 914 cm^{-1}indicated the bending vibration of the Al-O bond. Besides, the peak at 522 cm^{-1}belonged to the symmetric bending vibration of Si-O bond[17-19].

Compared with the infrared spectra of sodium-based MMT, it can be seen that the peaks at 522 cm^{-1}, 914 cm^{-1}, and 1039 cm^{-1}remained in the spectra of modified MMT.This result indicatedthe layered structure of MMT is preserved[20-21].

In addition, the peaks at 1635 cm^{-1}, 3442 cm^{-1}, and 3625 cm^{-1} in the infrared spectrum of the modified MMT were significantly weakened.This phenomenon indicated that the silane coupling agent had successfully graftedon the MMT surface. As a result, the number of hydroxyl groups reduced. In addition,the increasing in hydrophobicity within the layers leading to a decrease in adsorbed water. The increase in the peak area at 1039 cm^{-1} and 522 cm^{-1} indicatedthe increasingof Si-O-Si bonds, whichmight be caused by the introduction of a silane coupling agent. In the infrared spectra of KH550/MMT and KH570/MMT, there were N-H peak at 1606cm^{-1} and C=O peak at 1699 cm^{-1}, respectively. The stretching vibration absorption of -CH$_2$ and -CH$_3$were also indicated by peaksat 2921 cm^{-1} and 2852 cm^{-1}, respectively. Compared with the spectra of MMT, these two peaks in the spectra of modified MMT were obviously increased.This result strongly illustrates the introduction of the organic end caused by the successful grafting of the silane coupling agent[17,19,21-22].

The XRD pattern of MMT generally shows strong (001) crystal plane diffraction peaks. The XRD patterns of MMT modified by different coupling agents are shown in Figure 1(D). It can be seen from the figure that the (001) crystal plane diffraction peak of the unmodified MMT is at 5.14°.Therefore, the crystal plane spacing can be calculated from the Bragg equation to be about 1.719nm. After modification with a silane coupling

agent, the diffraction peaks of the (001) crystal plane of MMT moves to a lower angle. As a result, it can be inferred that the silane coupling agent inserted intoMMTlayers, which lead to an increase in the distance between the MMT layers[23-24].
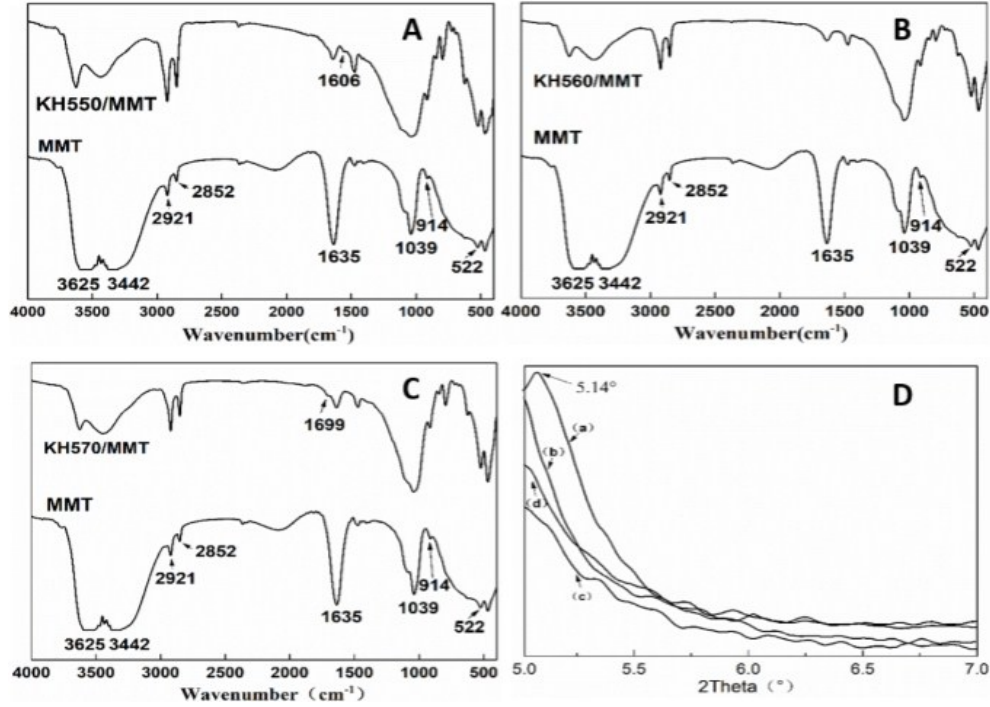

Fig 1   IRspectrum of MMT-550(A), MMT-560 (B), MMT-570 (C) and XRD pattern (D) of MMT (a), MMT-550(b), MMT-560 (c) and MMT-570 (d)

3.2 Effect of modifiers on the surface properties of MMT

This experiment was carried out with only adjustment of the amount of coupling agent when other related factors were controlled. Thecontact angle test results were used as the indicators to measure the effect of modification. The relationship between the amount of different coupling agents and the modification effect were shown in Figure 2(A). When the amount of the coupling agent is small, the hydroxyl groups on the surface of the MMT and the hydroxyl groups generated by the hydrolysis of the coupling agent undergo a condensation reaction or are adsorbed on the surface of the MMT by hydrogen bonding to form a coating layer. With the increasing of amount of the coupling agent, the coupling agent tends toself-gather and cause failure. As a result, the modification effect decreases[18-19]. It can be seen from the figure that the optimal modification concentrations of the three coupling agents KH550, KH560 and KH570 were 2%, 2% and 6% of the mass fraction of MMT, respectively. As shown in Figure 2(B), compared with the raw MMT, the contact angle test results of modified MMT prepared at the optimal modification concentrations of three coupling agents KH550, KH560, and KH570 increased by 20.69°, 22.96° and 27.98°, respectively.
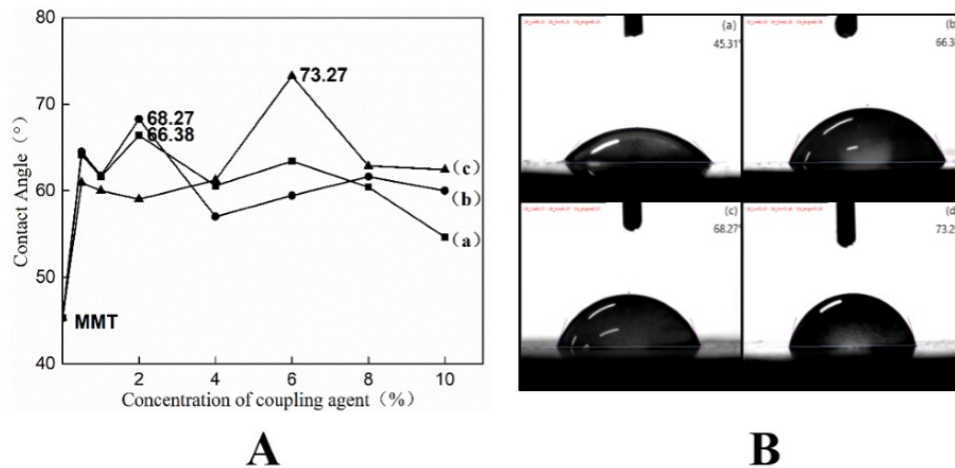
Fig 2   Contact anglesrelationship curves (A) between the amountof KH550 (a), KH560 (b),KH570(c) and contact angles photos (B)

3.3 Effect of solvent on the modification properties of modifiers

The effect of different solvents on the modification of the coupling agent was shown in Figure 3. By comparison, it can be concluded that pH and water has had different degrees of contribution to the modification effect of different coupling agents. It can be found that the presence of H^+ had a greater promotion on the modification effect of KH550 coupling agent. We speculated that H^+ can protonate the amino group of KH550 to form a quaternary ammonium cation[3-4]. The formed quaternary ammonium cationmight be easy to proceed exchange reaction with sodium ion in the MMT layer. This process can even strip the MMT sheet, as shown in Figure3. Compared with H^+, water did more contribution to the modification effect of KH560 and KH570 coupling agents. This result indicated that the modification mechanism of KH560 and KH570 is different from KH550. We speculated that compared to amino, epoxy and carbonyl are more difficult to combine with H^+. The presence of water can promote the hydrolysis of the organic end[5,8]. This effect might significantly improve the modification result, as shown in Figure3. After the polymer segment was inserted between the MMT layers, the MMT layer spacing is enlarged. The uniformity of the MMT dispersion in the matrix was improved. Allaspects of the performance of SBS were expected to be improved due the formation of uniform intercalated nanocomposite or exfoliated nanocomposite.
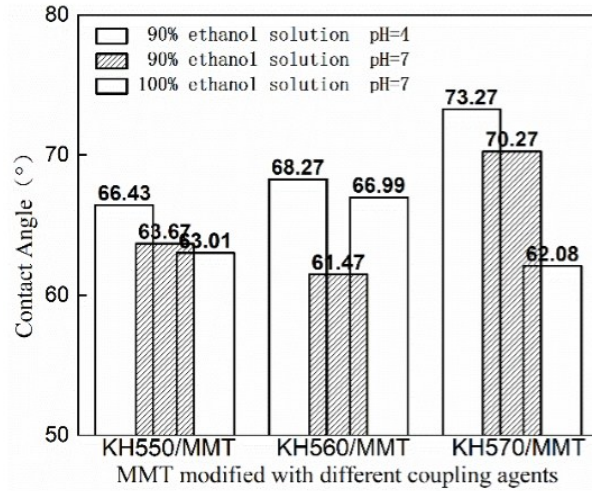
Fig 3　　Effect of different solvents on the modification

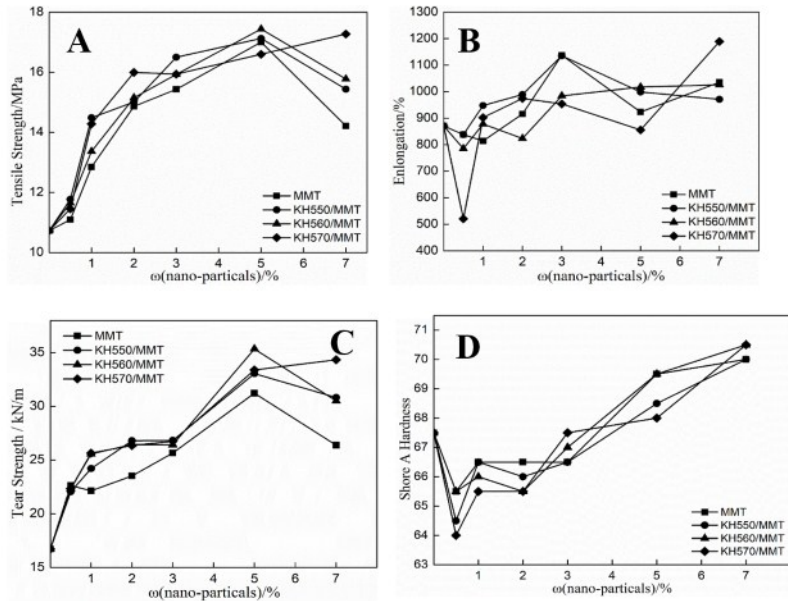## 3.4 Comprehensive mechanicalproperties of MMT/SBSnanocomposites

Fig 4　　Tensile properties (A), enlongation (B), tearproperties (C) and hardness (D) of MMT/SBS nanocomposites

It can be seen from Figure 4(A) that when less than 3% of inorganic powder was added, the enhancement effect of modified MMT on SBS is significantly better than that of unmodified MMT. Due to stronger binding force and improved force transmission between the modified MMT and elastomer, the mechanical properties of the SBS contained modified MMT are better than those with unmodified MMT. However,the addition of a large amount of inorganic powder lead to self-gather. These aggregates

cause the formation of defects in the polymer matrix,the mechanical properties of the composite will also decline. Therefore, when adding more than 5% of powder, the tensile strength of SBS with KH550, KH560 modified MMT and unmodified MMT decreased. In contrast, the mechanical properties of SBS with KH570 modified MMT still increased. This should be caused by the similarity ofthe double bonds structure in both the SBS structure and the organic part of KH570 silane coupling agent. Therefore, compared to the KH550 and KH560 silane coupling agents with larger organic ends, the KH570 silane coupling agent modified MMT is more soluble in SBS[25-27].

The elongation at break of a thermoplastic elastomer can be affected by the tensile strength of the polymer matrix, powder properties (including particle size and surface activity, etc), the amount used and its distribution[25]. As shown in Figure 4(B), when the content of the MMT in the elastomer matrix is less than 1 %, uniformly distributed MMTstrongly reinforcedthe SBS matrix. In addition, due to the largesurface MMT had in contact with the SBS matrix lead to strong interaction, the movement of the SBS molecular chain is hindered at room temperature. Therefore, when 0.5% of inorganic powder is added, the elongation at break was reduced. With the increase of the amount of addedpowderhinderedthe occurrence of fracture, the tensile strength of the SBS composite material was increased. However, when the SBS matrix is deformed, the increase in the interface causes the interface slip to increase. So as the amount of powder added was increased, the elongation at break increased.

As shown in Figure4(C), the SBS with less than 3% of modified MMT has a much higher tear strength improvement than that of SBS with unmodified MMT. As the increase of the amount of powder added, the aggregation of modified and unmodified MMT became prominent.This lead to the decrease of interface binding force. Large particles formed by the aggregation of MMT in the polymer matrix tend to become stress concentration points and defects in the SBS matrix. As a result the tear resistance of SBS is reduced again.

The relationship between the Shore A hardness and the amount of nano-powder is shown in Figure4(D). The Shore A hardness in the elastomer has a certain relationship with its Young's modulus, because the hardness is affected by the ability of segment movement. As the decrease of segment mobility worsens lead to the increases of Young's modulus, the hardness increases, and vice versa [26-27]. When less than 3% of powder was added, the insertion of polymer segment into MMT layer prevented the entanglement of SBS chains. Macroscopically, SBS deformation increases with when external stress accumulated. Microscopically,mobility of chain increases because of the change of environment. These changes resulted in the decrease of the stiffness of the SBS itself and the hardness of the material. TheYoung's modulus of the inorganic powder is much larger than that of the SBS elastomer. So it can also be seen from the figure thatthe Young's modulus of the composite material increases significantly with the increase of the amount of powder added. So the hardness increases accordingly.
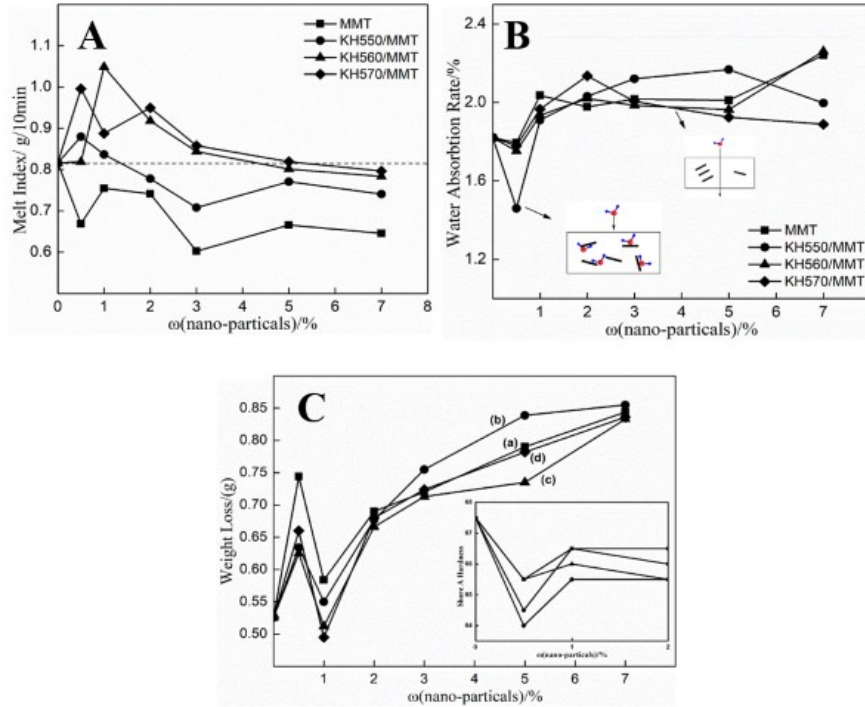
Fig 5　　Melt properties (A), absorbtion properties (B) andfrictionalproperties (C)of MMT/SBS nanocomposites

The relationship between the melt flow rate of the nanocomposite and the amount of nanopowder obtained in the experiment is shown in Figure 5(A). The addition of MMT makes the melt flow rate of SBS significantly decreased. So the processing performance of SBS suffers. The layered structure of MMT can hinder the flow of the melt. When modified MMTwas added in 3% or less, the melt fluidity is significantly improved. Then the melt fluidity becomes worse with the increase of the amount of modified MMT. However, it was basically being kept in the same level as SBS, which is significantlyhigher than SBS with unmodified MMT[27].

The size of the dispersed phase in the nanocomposite drops in nanoscal. The large specific surface area of the dispersed phase increase the interaction between the two phases. In the nanocomposite with good compatibility,the movement of the polymer surrounds the dispersed phase is restricted by the nano-particles. This structure making the nanometer composite materials have achieved good reinforcements[28-29]. It can be seen from Figure5(B) that with the increase of the amount of powder added, due to the aggregation of the powder, voids appear between the powder and the matrix.So the solvent resistance of SBS becomes worse. On the contrary, when 0.5% of powder was added, the solvent resistance properties of SBS were enhanced, which should be caused by the uniform dispersion of MMT and the peeling of a small number of sheets. Compared with the other two coupling agents, the addition of 0.5% of KH550 coupling agent

modified MMT has greatly improved the solvent resistance properties of SBS elastomer.This phenomena also supported that the cation exchange between KH550 coupling agent and sodium ions had occurred. The reaction, due to the large volume of KH550 molecule, is likely to cause a large amount ofMMT sheet to peel off and disperse in the SBS matrix, resulting in a significant increase in solvent resistanceproperties[29].

The effects of MMT and modified MMT on the wear properties of SBS are shown in Figure5(C). Combined with the changes in hardness mentioned above, when 0.5% of modified powder is added, the hardness of the nanocomposite material is significantly reduced, so the amount of wear was increased [30]; when the amount of modified powder is 1%, the hardness of modified MMT/SBSnanocomposite is basically the same as that of SBS.So the amount of wear is reduced and close to the amount of SBS. At this time, the wear resistance of the modified MMT-filled SBS was significantly better than that of the unmodified MMT. However, with the increase of the powder content, the problem of aggregation gradually becomes dominant and large particles was formed.Larger particles are more easily removed from the surface of the SBS than the smaller ones. As a result, macroscopically, the amount of wear was increased.

4. Conclusion

Three coupling agents of KH550, KH560 and KH570 were investigated as modifiers for MMT/SBS nanocomposites. Thereaction between MMT paritcles and modifiers was investigated. The organic coating layer and surface properties were observed in modified MMT. Together with theinteraction of modified MMT by modifiers and SBS chains during the processing, modifiers acted as an effective interfacial modifier to improve the dispersion of MMT in SBS matrix and strengthen the SBS-MMT interfacial bonding for the processing. The ultimate mechanical performance of the MMT/SBS nanocomposites in situ modified with modifiers was found to be largely improved. Among three coupling agentsÿthe effect of KH570 is more pronounced.

Acknowledgments

Reference

[1] Pu M F, Liu M T. Progress of the organic modifiers in polymer/clay nanocomposites, Polymer Materials Science and Engineering, 2010,26(12):168-172. Chinese

[2] Liu Y Q, Mo X Z. Study on properties of SBS/PS/nano-MMT composites, China Elastomerics,

2014,24(3):12-14.Chinese

[3]   Yu C C, Ke Y C, Hu X, et al. Effect of bifunctional montmorillonite on the thermal and tribological properties of polystyrene/montmorillonite nanocomposites. Polymers, 2019, 11(5): 834-840.

[4]   Zhao Z N, Liang L S, Lv A L. Study on the coupling agent treatment on the needle-like wollastonite and polypropylene composite, China Plastics Industry, 2014,42(12):87-92.Chinese.

[5]   Zhang C Y, Luo J X, Wu H, et al. Influence of temperature and ratio of coupling agent on nano-TiO_2 surface modification, New Chemical Materials, 2016,44(2):232-234. Chinese

[6]   Wang F Z, Li M, Qu Z Y, et al. Improvement of the FRP sheet bonded to concrete substrate by silane coupling agent, Journal of Wuhan University of Technology-Materials Science Edition. 2018, 23(1):117-123.

[7]   Lin C, Hu W, Wan X D, et al. Fabrication and performance of SBS/EVA hot-melt adhesive, Journal of Materials Scicence and Engineering, 2018, 36(6):879-883.Chinese

[8]   Zha C, Wang W, Lu Y, et al. Constructing covalent interface in rubber/clay nanocomposite by combining structural modification and interlamellar silylation of montmorillonite, ACS Applied Materials and Interfaces, 2014, 6(21): 18769-79.

[9]   Hafezi S M, Enayati A, Hosseini K D, et al. Use of amino silane coupling agent to improve physical and mechanical properties of UF-bonded wheat straw(Triticum aestivum L.) poplar wood particleboard, Journal of Forestry Research. 2016, 27(2): 427-431.

[10] Luo W C, Wang X, Huang R H, et al. Interface enhancement of glass fiber/unsaturated polyester resin composites with nano-silica treated using silane coupling agent, Wuhan University Journal of Natural Sciences . 2014, 19(1): 34-40.

[11] Ye L Z, Liu X M, Zhu Y H, et al. Study on the processing and the properties of thermoplstic elastomer, Plastics Science and Technology,1998,3:26-29.Chinese

[12] Choi W K, Park G Y, Kim B S, et al. Effect of silane coupling agent on the creep behavior and mechanical properties of carbon fibers/acrylonitrile butadiene rubber composites. Journal of Nanoscience and Nanotechnology, 2018, 18(9): 6220-6227

[13] Wang X D, Yun S N, Zhang T H, et al. Advances in basalt fiber-reinforced composites modified by silane coupling agent, Materials Review, 2017,31(3):77-85.Chinese

[14] Zhang H, Zheng J P, Gao H, et al. In vitro biodegradation and biocompatibility of gelatin/montmorillonite-chitosan intercalated nanocomposite. Journal of Materials Science: Materials in Medicine, 2007, 18(5): 951-957.

[15] Salarizadeh P, Javanbakht M, Pourmahdian S, et al. Surface modification of Fe_2TiO_5 nanoparticles by silane coupling agent: Synthesis and application in proton exchange composite membranes. Journal of Colloid and Interface Science, 2016, 472:135-44.

[16] Zheng J P, SU Q, Wang C, et al. Synthesis and biological evaluation of PMMA/MMT nanocomposite as denture base material. Journal of Materials Science: Materials in Medicine, 2011, 22(4): 1063-1071.

[17] Chen, W W, Wu S W, Lei YD, et al. Interfacial structure and performance of rubber/boehmitenanocomposites modified by methacrylic acid. Polymer. 2011, 52: 4387-4395.

[18] Tai Y L, Qian J S, Miao J. B, et al. Preparation and characterization of Si3N4/SBR nanocomposites with high performance. Materials & Design, 2012, 34: 522-527.

[19] Xia R, Li M H, Zhang Y C, et al. Synthesis of tercopolymer BA–MMA–VTES and surface modification of nano-size Si3N4with this macromolecular coupling agent, Journal of Applied Polymer Science, 2008, 107:1100-1107.

[20] Jackson A W, Shebanova O, Hector A L, et al. Amorphous and nanocrystalline titanium nitride and carbonitride materials obtained by solution phase ammonolysis of Ti(NMe2)4, Journal of Solid State Chemistry, 2006, 179: 1383-1393.

[21] Zhou X S, Peng F, Wang H J, et al. Preparation of nitrogen doped TiO2 photocatalyst by oxidation of titanium nitride with H2O2, Materials Research Bulletin, 2011, 46: 840-844.

[22] Chen D, Li J H. Interfacial functionalization of TiO2 with smart polymers: pH-controlled switching of photocurrent direction, the Journal of Physical Chemistry C, 2010, 114: 10478-10483.

[23] Li X Y, Ding F C, Zhang H Q, et al. Study on preparation and properties of VAE/MMT nanocomposite barrier coatings,China Plastics, 2019,33(10):1-5.Chinese

[24] Wu S H, Zhang H, Zhang L. Reinforcement-flame retardant mechanism of CTAB-SCA modified Na-montmorillonite/rubber composites, Acta Materiae Compositae Sinica,2019, 36(11): 2710-2717. Chinese

[25] Guo B C, Lei Y D, Chen F, et al. Styrene–butadiene rubber/halloysite nanotubes nanocomposites modified by methacrylic acid, Applied Surface Science, 2008, 255: 2715-2722.

[26] Guo B C, Chen F, Lei Y D, et al. Styrene-butadiene rubber/halloysite nanotubes nanocomposites modified by sorbic acid, Applied Surface Science , 2009, 255: 7329-7336.

[27] Rooj S, Das A, Thakur V, et al. Preparation and properties of natural nanocomposites based on natural rubber and naturally occurring halloysite nanotubes, Materials & Design, 2010, 31: 2151-2156.

[28] Carli L N, Roncato C R, Zanchet A, et al. Characterization of natural rubber nanocompositesfilled with organoclay as a substitute for silica obtained by the conventional two-roll mill method, Applied Clay Science, 2011, 52: 56-61.

[29] Wang Z B, Zhang Y X, Du F L, et al. Thermoplastic elastomer based on high impact polystyrene/ethylene-vinyl acetate copolymer/waste ground rubber tire powder composites compatibilized by styrene-butadiene-styrene block copolymer. Materials Chemistry and Physics, 2012, 136:1124-1129.

[30] Jayalatha G, Kutty S K N. Effect of short nylon-6 fibres on natural rubber-toughened polystyrene, Materials & Design, 2013, 43: 291-298.