Research Article

Preparation and Properties of KH-550 Modified Nano-SiC/Waterborne Polyurethane Composites

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ABSTRACT

As the nano-SiC has high hardness, high thermal conductivity, elastic modulus, excellent wear resistance and other properties, In this study, the use of nano-SiC as a reinforcing agent. The nano-SiC was wrapped via the method of reflux by KH-550 (γ-aminopropyltriethoxysilane), the SiC can be better dispersed in waterborne polyurethane, synthetic KH-550 modified SiC/ waterborne polyurethane composites. By using FI-IR, XRD, SEM, TG, universal testing machine to test the analysis. Experiments show that nano-SiC can improve the mechanical properties of waterborne polyurethane and KH-550 modified nano-SiC is more significant than the nano-SiC, simultaneously adding KH-550 modified nano-SiC/waterborne polyurethane composites than waterborne polyurethane thermal conductivity increased.

Keywords: Nano-SiC; KH-550(γ-aminopropyltriethoxysilane); Waterborne polyurethane mechanical property; Thermal conductivity

Introduction

Polyurethane (PU) is referred polycarbamate and within it contains a large amount of carbamate.[1] Waterborne polyurethane is a water-soluble or water-dispersible polyurethane resin.[2-5] Waterborne polyurethane (WPU) contains small amount of organic solvent and thus, does very little harm to environment.[6] In 1849, German Woods synthetic aliphatic isocyanates,[7] in 1937, Bayer and his colleagues first synthesized polyurethane resin,[8] industrialization in 1944, in 1967, DuPont achieved the first industrial waterborne polyurethane,[9] after this point, Europe and Japan for research and development of waterborne polyurethane very seriously,[10] however, compared with solvent-based PU, it has the characteristics of environmental protection, energy saving, safety and excellent performance, it is a rapidly developing green materials and used in various industries.[11] Waterborne polyurethane (WPU) has the advantages of no pollution, good adhesion, wear resistance, low temperature resistance, good flexibility and so on.[12] But its mechanical properties will change at a certain temperature.

Nano-SiC is an excellent semiconductor material and it has a high thermal conductivity, oxidation resistance and high mechanical strength and chemical resistance. But the phenomenon of agglomeration of nano-SiC, which makes it difficult to present the nano particles in the resin, therefore, firstly, the surface modification of nano-SiC was carried out, coupling agent which can be connected with resin by grafting on the surface and Better dispersed in the resin.[13] Yekai certain proportion KH-560 modified nano-SiC is added to the epoxy resin and found that the tensile strength of the composites increased by 5% and heat resistance increased by 80.65%.[14]

In this study, silane coupling agent KH-550 was grafted onto the surface of nano-SiC and modified nano-SiC was mixed with waterborne polyurethane to form KH-550 modified nano-SiC/ waterborne polyurethane composite and heat resistance and mechanical properties of the composites were discussed.

Experimental Details

Materials

Nano-SiC(Shanghai Aladdin Reagent Co. Ltd.) with particle size of 150 nm and its specific surface area is 17.9562 m^2/g toluene diisocyanate (TDI, Tokyo Chemical Industry Co. Ltd.); ethanol (Shanghai revitalization of the first chemical plant); triethylamine and 1,2-ethylenediamine (EDA) were products of Chinasun specialty Co. Toluene, Acetone, hydrochloric acid (1 mol/l)were received from Shanghai Su Yi Chemical Reagent Co. Di-n-butyltin dilaurate (China West Asia Reagent Co. Ltd.); distilled water directly from the laboratory. N-methylpyrrolidone (NMP), glycol (EG), polypropylene glycol 2000 (PPG2000) were obtained from Sinopharm Chemical Reagent Co, PPG2000 and DMPA was dried under vacuum at 120°C for 12 h. Silane coupling agent KH-550, dibutylamine titration, tbromcresol green, dimethylolpropionic acid (DMPA) were all products of Shangh Aladdin Reagent Co. NMP, EG, TEA, acetone were distilled and kept on a 4A molecular sieve before use.

Instrument

DF-101B collector-type magnetic heating stirrer (Jintan Medical Instrument Factory); FI-IR (FTS2000); XRD (Shimadzu XRD-6000); SEM (INCA); TG (Pyris Diamond); WDW-50 Composite Universal Testing Machine (Shanghai Rui Yu Equipment Co. Ltd.).

Experimental procedure

Preparation of KH-550 modified nano-SiC: Quantitative nano-SiC was dried at 200℃ for 12 h. After the drying of nano-SiC, proper amount of toluene and the corresponding ratio of silane coupling agent KH-550 were added into a 250 ml three-neck flask equipped with a magnetic stirrer, thermometer, condenser and nitrogen gas inlet and heated at 95°C with stirring for 6 h. After the reaction, and take advantage of heat filtration, dissolved in distilled water and ultrasonic dispersion, after ultrasonic dispersion, centrifuged twice with distilled water, and then dissolved in acetone and ultrasonic dispersion, after ultrasonic dispersion, centrifuged twice with acetone. Finally, the product was collected and dried in an oven at 105°C for 12 h. After cooling to room temperature, weighing and grinding. Since siloxane in silane coupling agent is the main group that reacted with hydroxyl groups on the nano-SiC surface and it is easy to hydrolysis,[15] so the reaction must be carried out in the anhydrous alcohol. Therefore the experiments solvent selected toluene.

Preparation of waterborne polyurethane: Firstly, quantitative PPG2000 and DMPA were dried in a vacuum oven at 120℃ for 2 h. The toluene diisocyanate is added into a 250 ml four-nect flask equipped with a mechanical stirrer, thermometer, condenser, then the flask was added to PPG2000, and heated at 70°C with stirring for 2 h to obtain a homogeneous mixture, then, DMPA dissolved in NMP were added into four-neck flask equipped and added to 3 to 4 drops di-n-butylamine dilaurate (DBTDL), maintaining the temperature and the reaction was continued for 2 h. EG was added into the mixture until the NCO content reached the theoretical value to produce NCO-terminated pre-polymer I, maintaining the temperature and the reaction was continued for 1.5 h. The NCO content was monitored via a standard dibutylamine titration method.[16] Because of the high viscosity of prepolymer I, a suitable amount of acetone was added to dilute the reaction system. When the NCO content reached the theoretical value to produce NCO-terminated prepolymer II. TEA as neutralizing reagent (according to the molar ratio TEA: DMPA=1.2:1) was not added into the reaction until the mixture was slowly cooled to 40°C, and the reaction was continued for 0.5 h. Finally, distilled water and EDA were not added into the reaction until the mixture was slowly cooled to room temperature, and agitation at high shearing rates to emulsify the solution for 0.5 h. Then the acetone of waterborne polyurethane emulsion was reduced by vacuum distillation and the waterborne polyurethane emulsion without acetone was obtained.

Preparation of KH-550 modified nano-SiC/waterborne polyurethane composites films: Firstly, KH-550 modified nano-SiC grinding into powder, quantitative KH-550 modified nano-SiC dissolved in NMP was added into a 100 ml beaker equipped and ultrasonic dispersion. Then WPU was added to the 100 ml beaker equipped with stirring. The KH-550 modified nano-SiC/WPU mixture was then thoroughly mixing. Finally, it is injected into a mold of PTFE plate and films at room temperature for 7 days. In order to observe temperature resistance and mechanical properties of KH-550 modified nano-SiC/WPU composites, we also prepared unmodified SiC/WPU composites and WPU blank samples. Finally, through the thermal gravimetric analyzer and universal testing machine to test the temperature resistance and tensile strength.

Results and Discussion

Analysis of FTIR

The structure of nano-SiC and KH-550 modified nano-550 was confirmed by FTIR spectroscopy. FTIR spectra of nano-SiC (a) and KH-550 modified nano-SiC (b) are shown in Figure 1. The FTIR spectrum of nano-SiC and KH-550 modified nano-SiC showed the strong absorption peaks at 900 cm^{-1} [ν(SiC)] and it is the most basic absorption peak of nano-SiC. The characteristic peaks of adsorbed water on SiC surface at 3760 cm^{-1} and 1560 cm^{-1}. The characteristic absorption peaks corresponding to KH-550 modified nano-SiC could be observed clearly at 1300 cm^{-1} [δ(CH)], 1122cm^{-1} and 1033 cm^{-1} [ν(SiOSi)]. This last two characteristic peaks can also be observed in the spectrum of KH-550 modified nano-SiC, because the two characteristic peaks corresponds to Si-O-Si produced by the reaction of the hydroxyl groups on the surface of the nano-SiC and the alkoxy of KH-550 end. Then the -NH_2 on the KH-550 absorption peak at about 2930 cm^{-1} disappeared in the spectrum, showing that KH-550 has successful grafting onto the surface of nano-SiC by reaction.

Analysis of XRD

The surface structure and composition of nano-SiC and KH-550 modified nano-SiC were analyzed by X-ray diffraction, and the JCPDS method was used to identify the surface structure and composition. The X-ray diffraction of nano-SiC and KH-550 modified nano-SiC is shown in Figure 2. The different crystal faces of nano-SiC were displayed in the Figure 2A that it is (111),(200),(220),(311)和(222). But the lattice plane appeared in Figure 2B was same as Figure 2A and the intensity of each peak is similar to the intensity of each peak in Figure 2A, showing that the structure and chemical composition of nano-SiC has not changed after the surface modification by Silane coupling agent KH-550.

Analysis of electron microstructure

Scanning electron microscopic (SEM) analysis of KH-550 modified nano-SiC particle: Figure 3 shows SEM image of

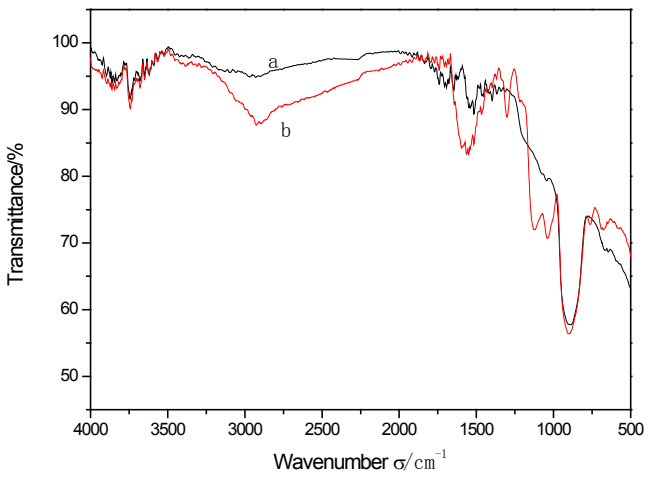

Figure 1: FTIR spectra of nano-SiC (a) and KH-550 modified nano-SiC (b).

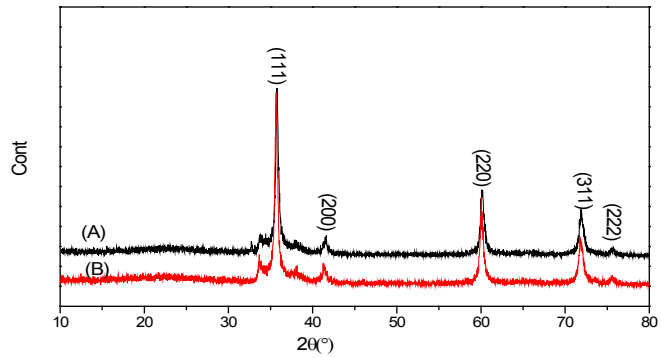

Figure 2: XRD pattern of: (A) nano-SiC and (B) KH-550 modified nano-SiC.

nano-SiC and KH-550 modified nano-SiC. Nano-SiC particles showed irregular shapes in Figure 3A, then the formation of accumulation and the larger gap between the particles, and there is a large gap between the accumulation, aggregate formation between the particles and there is an obvious phenomenon of agglomeration, this is due to the small diameter of the nano-SiC and the nano-SiC surface has a large number of polar hydroxyl groups and quantitative surface energy, so that the particles agglomeration together; However, KH-550 modified nano-SiC showed uniform distribution in Figure 3B, small voids between the particles and surface smooth, there is no accumulation and aggregation phenomenon between the particles, the organic group was grafted on the surface of KH-550 modified nano-SiC in Figure 3, the interaction between molecules separate the particles, thus inhibiting the phenomenon of agglomeration. From here we see that surface modification of nano-SiC by KH-550 can obviously reduce the phenomenon of agglomeration, the KH-550 modified nano-SiC particles with uniform distribution and small voids can be obtained.

Scanning electron microscopic (SEM) analysis of KH-550 modified nano-SiC/WPU composite films: Figure 4 shows SEM image of WPU, 0.5% nano-SiC/WPU composite and 0.5% KH-550 modified nano-SiC/WPU composite. The waterborne polyurethane showed smooth in Figure 4A, however bright spot may be dust or other fine powder in nature in Figure 4A. Nano-SiC/WPU composite showed lots of bright spots with different shapes and uneven distribution in Figure 4B, this is due to the nano-SiC surface has a large number of polar hydroxyl groups and quantitative surface energy, which leads to the accumulation of particles, therefore, the compatibility between nano-SiC and waterborne polyurethane is poor and appear reunion in the matrix. KH-550 modified nano-SiC/WPU composite showed lots of bright spots and uniform distributed in Figure 4C, this is due to reaction between KH-550 and hydroxyl group on the surface of nano-SiC, then the organic group was grafted on the surface of nano-SiC, the interaction between molecules separate the particles, therefore, the phenomenon of agglomeration will not occur, this makes the KH-550 modified nano-SiC can be better dispersed in waterborne polyurethane matrix. From here we see that KH-550 modified nano-SiC dispersed more evenly in waterborne polyurethane matrix and will not be phenomenon of agglomeration, it is also demonstrated that the KH-550 modified nano-SiC/WPU composites have excellent mechanical properties.

Analysis of TG

Figure 5 and Table 1 were the thermogravimetric (TG) and thermal weight loss rate of WPU, nano-SiC/WPU composite materials (0.5%) and KH-550 modified nano-SiC/WPU (0.5%) composite materials, respectively. As shown in Figure 5, the initial decomposition temperature of WPU and nano-SiC/WPU composite were 200°C, 210°C, respectively, which improved 10°C. This can be attributed to the temperature resistance of nano-SiC. After compounded with WPU, it was play a certain role in the improvement of initial decomposition temperature of composite materials. But it was not deadly obvious because the dispersion of nano-SiC in the aqueous polyurethane was poor. The initial decomposition temperature of KH-550 modified nano-SiC/WPU composite was 222°C which increased 22°C. In order to make the nano-SiC evenly dispersed in aqueous polyurethane, the modification of nano-SiC was taken before dispersed. As a result, the initial decomposition temperature of KH-550 modified nano-SiC/WPU composite displayed an increase. The termination temperature of WPU, nano-SiC/WPU composite and KH-550 modified nano-SiC/WPU composite are shown in Figure 5. Compared with WPU, the termination temperature of nano-SiC/WPU composite and KH-550 modified nano-SiC/WPU composite was enhanced about 8°C, 23°C, respectively. The KH-550 modified nano-SiC dispersed in the waterborne polyurethane evenly, then a space network structure formed between the hydroxyl groups on the surface of nano-SiC and the waterborne polyurethane by grafting chemical cross-linking reaction, which can be improved the temperature properties of the composites. As illustrated in Table 1, changes in thermal mass loss rate and temperature were uneven for different types of waterborne polyurethane (WPU, 0.5% nano-SiC/WPU and 0.5% KH-550 modified nano-SiC/WPU). It displayed a maximum mass loss rate for them. It was found that the maximum mass loss rate of WPU, nano-SiC/WPU and KH-550 modified nano-SiC/WPU were 1.54%/°C, 1.0%/°C, 1.28%/°C, which the temperature were at 270°C, 279°C, 295°C, respectively. For nano-SiC/WPU composite when the temperature was arrived at 575°C, the quality was no longer decreased; but for KH-550 modified nano-SiC/WPU composite, 590°C, the quality was no longer reduced until 590°C. It was indicated that the decomposition of waterborne polyurethane film was complete. By comparing with the temperature under same mass loss rate (Table 1), it was suggested that WPU corresponded to high temperature at the low rate of mass loss; while KH-550 modified nano-SiC/WPU composite material corresponded to high temperature at the high rate of mass loss. This is due to changes in the spatial structure between hydroxyl group on the surface of KH-550 modified

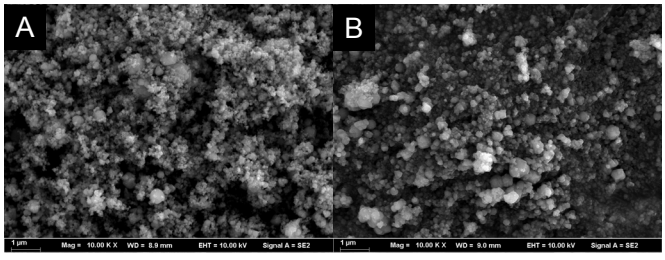

Figure 3: SEM image of: nano-SiC (A) and KH-550 modified nano-SiC (B).

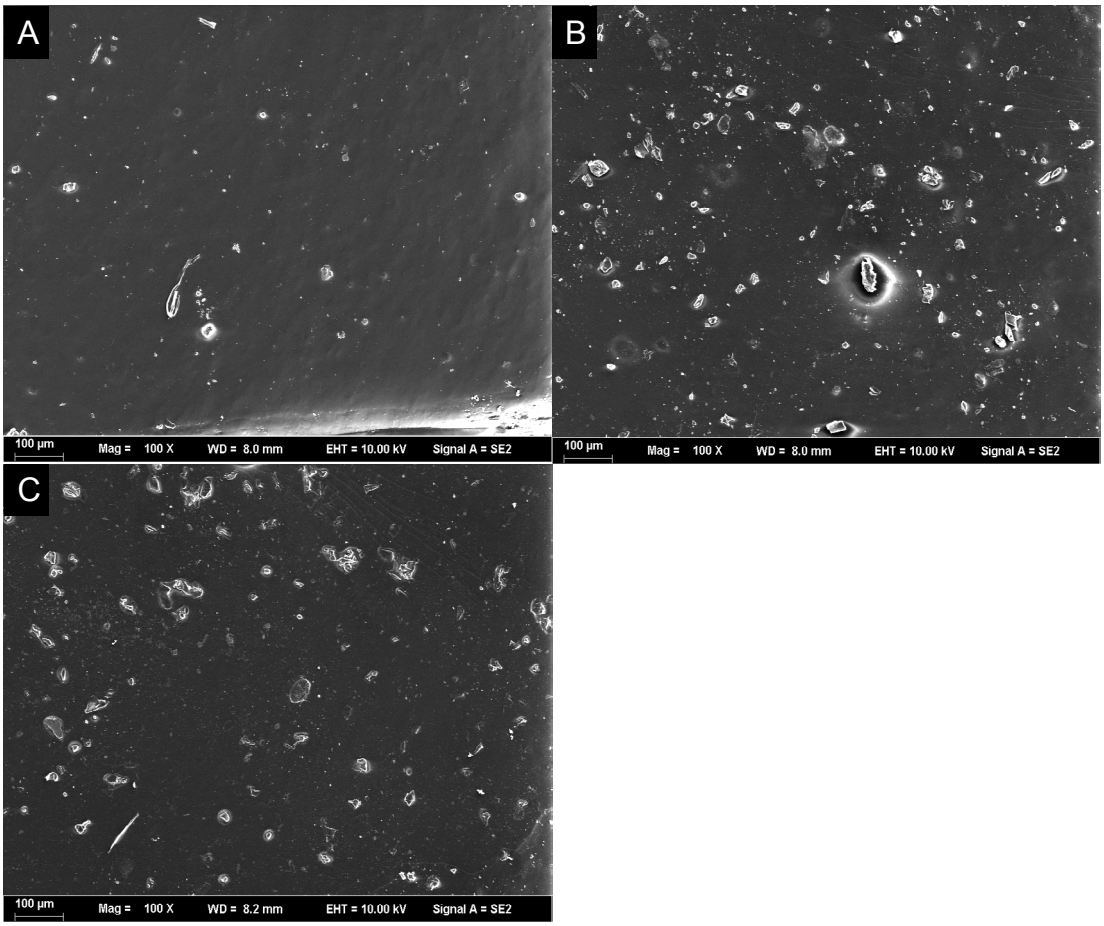

Figure 4: SEM image of: WPU (A); 0.5% nano-SiC/WPU composite (B) and KH-550 modified nano-SiC/WPU composite (C).

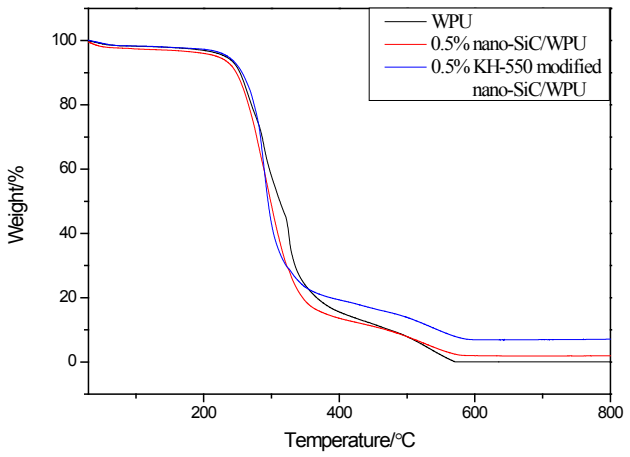

Figure 5: Thermogram curves of different types of waterborne polyurethane films (WPU; 0.5% nano-SiC; 0.5% KH-550 modified nano-SiC/WPU).

nano-SiC and waterborne polyurethane. The results showed that the temperature resistance of KH-550 modified nano-SiC/WPU composite was improved from the whole process of mass loss.

Dispersion analysis of different types of waterborne polyurethane films

In this study, nano-SiC modified waterborne polyurethane composites were prepared, and nano-SiC were mixed with waterborne polyurethane emulsion and distribution was observed in WPU. Figure 6 shows the film of WPU and the films of the same quality nano-SiC/WPU composite and KH-550 modified nano-SiC/WPU composite. Figure 6A shows the film of WPU and smooth film. Figure 6B shows preparation of the film by mixing with nano-SiC and waterborne polyurethane shows that nano-SiC is not completely dispersed in the film, agglomeration and irregular and not smooth. Figure 6C shows preparation of the film by mixing with KH-550 modified nano-SiC and waterborne polyurethane, KH-550 modified nano-SiC is completely dispersed and smooth surface in the WPU. The above analysis shows that KH-550 modified nano-SiC is better dispersion than nano-SiC in waterborne polyurethane, because the surface grafting coupling agent molecule group can react with the group in the waterborne polyurethane, So that KH-550 modified nano-SiC can be better dispersed in waterborne polyurethane.

Mechanical properties of KH-550 modified nano-SiC/WPU composites

Figure 7 shows extensibility percentage and tensile strength of the composite that is different content of KH-550 modified nano-SiC and waterborne polyurethane. The tensile strength of the composite is increases with content of KH-550 modified nano-SiC and the extensibility percentage was contrary in Figure 7. Figures 8 and 9 were the tensile strength and extensibility percentage of different WPU composite material, wherein the sample 1 was waterborne polyurethane, the sample 2 was nano-SiC/WPU composite and the sample 3 was KH-550 modified nano-SiC/WPU composite. The tensile strength of sample 2 and 3 were obviously increased in Figure 8. The tensile strength

Table 1: Thermal weight loss rate of different types of waterborne polyurethane films (WPU;0.5% nano-SiC;0.5% KH-550 modified nano-SiC/WPU).

Project	Thermal weight loss rate /%								
		10	20	30	40	50	60	70	80	90
temperature/℃	WPU	253	270	287	297	312	326	334	368	474
	0.5% nano-SiC/WPU	249	269	279	289	299	309	322	346	475
	0.5% KH-550 modified nano-SiC/ WPU	256	275	284	289	295	303	322	387	548

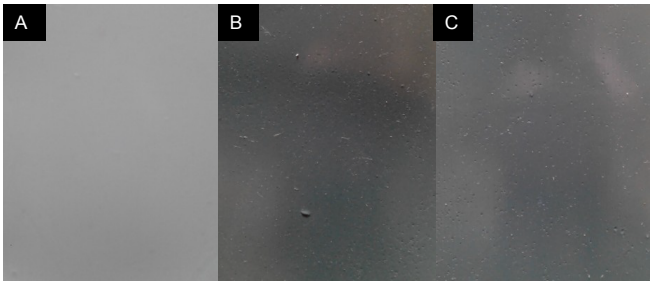

Figure 6: The films dispersion analysis of: WPU (A); nano-SiC/ WPU (B); KH-550 modified nano-SiC .

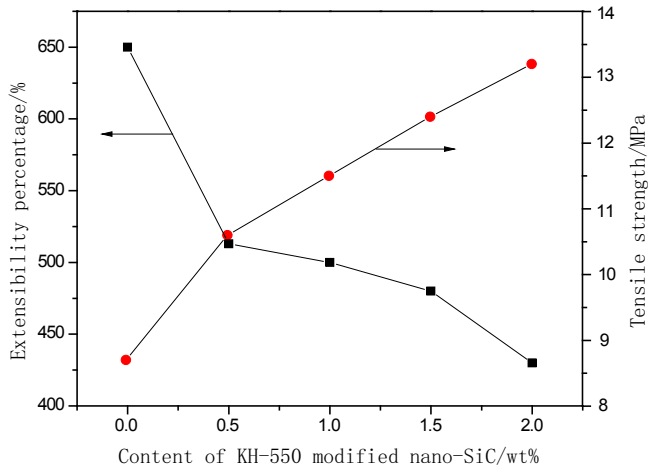

Figure 7: Effect of KH-550 modified nano-SiC content on extensibility percentage and tensile strength of composites.

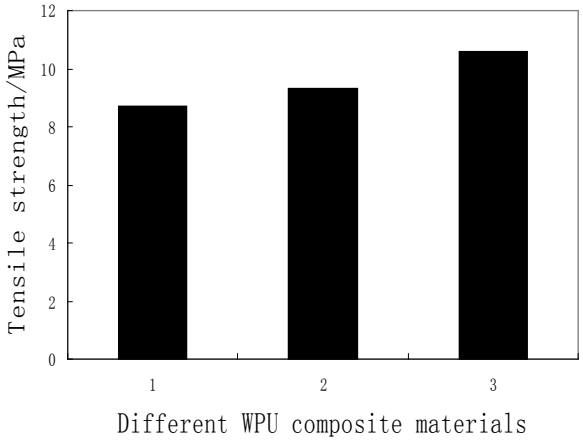

Figure 8: Relationship of different WPU composite material and tensile strength.

of KH-550 modified nano-SiC/WPU composite is better than nano-SiC/WPU composite in Figures 7 and 8, this is due to the reaction of silane coupling agent and the surface of nano-SiC

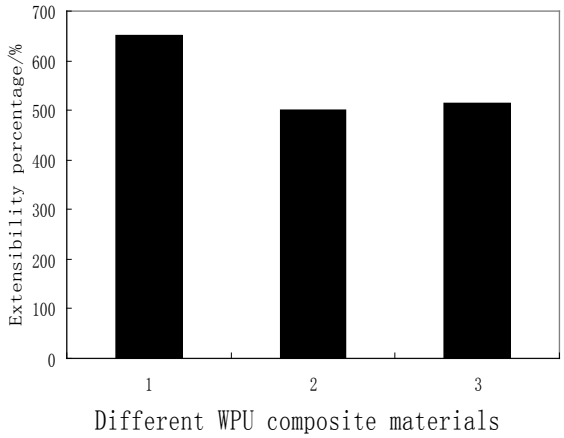

Figure 9: Relationship of different WPU composite material and extensibility percentage.

,then the organic group was grafted on the surface of nano-SiC, KH-550 modified nano-SiC can be better dispersed in waterborne polyurethane, and nano-SiC has the characteristics of high hardness, this is that the tensile strength of KH-550 modified nano-SiC/WPU composite is better than nano-SiC/ WPU composite. The extensibility percentage of sample 2 and sample 3 were significantly lower than sample 1 in Figure 9, but the extensibility percentage of sample 3 was better than sample 2. The extensibility percentage of KH-550 modified nano-SiC/WPU composite is better than nano-SiC/WPU composite in Figures 7 and 9, but the extensibility percentage of composite were lower than waterborne polyurethane, this is due to the high hardness characteristics of nano-SiC and adding to the waterborne polyurethane which made the hardness of waterborne polyurethane become larger, therefore the tensile strength of the composite become larger and the extensibility percentage become smaller.

Conclusion

In the word, the mechanical properties of KH-550 modified nano-SiC/WPU composite have been enhanced. The surface of nano-SiC has appear with group of silane coupling agent, show silane coupling agent was grafted on the surface of nano-SiC by FI-IR analysis test. KH-550 modified nano-SiC does not change the structure and chemical composition of nano-SiC by XRD analysis test. KH-550 modified nano-SiC and the compatibility of waterborne polyurethane is better than nano-SiC and the compatibility of waterborne polyurethane and it is not easy to reunite and uniform distribution by SEM analysis test. The thermal decomposition performance of KH-550 modified nano-SiC and waterborne polyurethane composites were superior by TG analysis test. When the amount of KH-550 modified nano-SiC and nano-SiC were same, the tensile strength and

extensibility percentage of KH-550 modified nano-SiC and water-borne polyurethane composites were significantly better than nano-SiC and waterborne polyurethane composites, thus the toughness and hardness of the KH-550 modified nano-SiC and waterborne polyurethane composite were better. But compared with waterborne polyurethane, the tensile strength of the composite is increases with content of KH-550 modified nano-SiC, however, the extensibility percentage of the composite is reduces with content of KH-550 modified nano-SiC.

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