Wuhan University
Journal of Natural Sciences

2014, Vol.19 No.1, 034-040

Article ID 1007-1202(2014)01-0034-07
DOI 10.1007/s11859-014-0975-7

Interface Enhancement of Glass Fiber/Unsaturated Polyester Resin Composites with Nano-Silica Treated Using Silane Coupling Agent

□ LUO Weicai[1], WANG Xiao[1], HUANG Ronghua[2], FANG Pengfei[1†]

1. School of Physics and Technology, Wuhan University, Wuhan 430072, Hubei, China;

2. School of Power and Mechanical Engineering, Wuhan University, Wuhan 430072, Hubei, China

Abstract: Nano-silica treated with different kinds of coupling agent (KH550, A-143, A-151) was used to modify the surface condition of glass fiber, and then, the modified glass fiber/ unsaturated polyester resin (UPR) composites materials were prepared. Scanning electron microscopy (SEM), dynamic mechanical analysis (DMA), and impact test were used to characterize the composite materials' structure and properties. The morphology of composite materials shows that the adhesion between nano-silica and glass fiber is improved when silane coupling agent is added in. The DMA and impact test results show that silane coupling agent (especially KH550 and A-151) could effectively improve the composite's mechanical properties. When the dose of KH550 was 0.1% (m ∶ m), the storage modulus and impact strength reached the maximum.

Key words: silane coupling agent; unsaturated polyester resin (UPR); glass fiber; nano-silica

CLC number: TQ 323

Received date: 2012-12-26

Foundation item: Supported by the National Natural Science Foundation of of China (J1210061)

Biography: LUO Weicai, male, Master candidate, research direction: polymer material. E-mail: lwc210@126.com

† To whom correspondence should be addressed. E-mail: fangpf@whu.edu.cn

0 Introduction

Glass fiber reinforced unsaturated polyester resin (UPR) composite materials have become the alternatives of conventional structural materials, such as wood and steel in some applications, because of its good mechanical properties. Mechanical properties of fiber-reinforced UPR composites depend on the properties of the constituent materials, the nature of the interfacial bonds, the mechanisms of load transfer at the interphase，and the adhesion strength between the fiber and the matrix[1,2]. The goal of this paper is to improve the adhesion strength between the fiber and the matrix of the composites.

Adhesion strength between the fiber and the matrix can be attributed to some combination of the following phenomena: mechanical adhesion, adsorption and wetting, electrostatic attraction, and chemical bonding[3]. Then, several modification techniques are developed for improving the adhesion strength between the fiber and the matrix. Surface treatment of reinforcement is a common method to improve adhesion properties by increasing electrostatic interactions or facilitating chemical bonding between the reinforcement material and the matrix[4-10]. Silane coupling agents, which are generally considered as adhesion promotors between fillers and the matrix, are widely used in the surface treatment of the reinforcement process.

Nanometer-sized materials as a reinforcement also

improved the adhesion between the fiber and the matrix. Wang *et al*[11] found out that the glass fiber/vinyl ester composites containing multiwalled carbon nanotubes (MWCNTs) showed better bonding between the glass fiber and the resin matrix. Many researchers[12-14] analyzed the effect of the nano-silica on the performance of the composites. However, they did not discuss the influence of the nano-silica on the interface cohesiveness of the composites. Although Zheng *et al*[15] prepared the SiO_2-glass-fiber epoxy composites to study the influence of nano-silica on the mechanical properties, they did not consider the effect of the addition of coupling agents.

In this study, different kinds and amount of coupling agents were used to modify nano-silica. Glass fiber was modified by the same amount of the modified nano-silica. Then, the modified glass fiber/UPR composite material was prepared. By comparing composite materials' macroscopic properties and microstructure before and after the addition of the nano-silica treated with coupling agents, we knew the relationship between the kind and dose of coupling agent and composite materials' performance.

1 Experimental

1.1 Materials

Unsaturated polyester resin (A407-901) was provided by the Nanjing Jinling DSM Resins Co., Ltd. Glass fiber (the ECR 469L-2400) was purchased from Chongqing Polycomposites International Co., Ltd. The nano-silica was purchased from Hubei Wuhan University Silicone New Material Co., Ltd. Methyl ethyl ketone peroxide and cobalt naphthenate were used in this experiment. The coupling agents used in this experiment were γ-aminopropyl-triethoxysilane (KH550), Vinyl-triethoxysilane (A-151), and γ-chloro-propyl trimethoxy silane (A-143). The molecular formula is shown in Fig.1.

1.2 Sample Preparation

Nano-silica was pretreated with different kinds and amount of siliane coupling agent. Then, the glass fiber was modified by means of the pretreated nano-silica and then dried and pruned. A certain amount of A407-901, methyl ethyl ketone peroxide, and cobalt naphthenate were mixed with the modified glass fiber into the mold. The mold was kept at 100 ℃ for 1 h to prepare the samples. Coupling agents' type and content relative to glass fiber (%, $m:m$) are shown in Table 1. The sample of No.1 was the composite materials, for which the glass fiber was not pretreated.

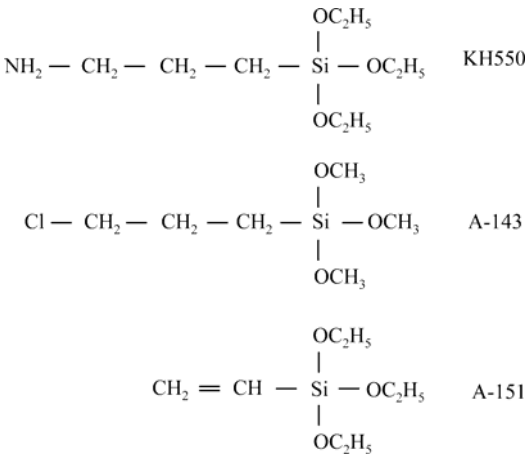

Fig. 1 Molecular formula of γ-aminopropyl-triethoxysilane (KH550), Vinyl-triethoxysilane (A-151), and γ-chloro-propyl trimethoxy silane (A-143)

Table 1 Dose of the reinforcement

Sample	Coupling agent	Dose of reinforcement/%
1	control	—
2	KH550	0.10
3	KH550	0.25
4	KH550	0.50
5	A-143	0.10
6	A-143	0.25
7	A-143	0.50
8	A-151	0.10
9	A-151	0.25
10	A-151	0.50

1.3 Sample Characterization

1) Scanning electron microscopy (SEM) analysis. The morphology of samples with cryogenically fractured surface under liquid nitrogen was examined with FEI Sirion-FEG.

2) The dynamic mechanical test. NETZSCH DMA 242C was used for dynamic mechanical analysis. The operation condition: heating rate 2 ℃/ min, the vibration frequency 1Hz, and scan range from 25 ℃ to 180 ℃.

3) Impact test. The tests were performed according to GB2571-81 at room temperature using with an impact tester (MZ-2054) made by Jiangdu Pearl Test Machinery Factory.

2 Results and Discussions

2.1 The Morphology of Glass Fiber before and after Modification

During the formation of the interface layer, the fiber and the matrix usually experience the process of contact

and wetting. The wetting performance of the interface depends on the size of the area where the fiber and the matrix attract from each other[16]. The fiber always attracts these components, which reduce their surface energy, and the maximum is preferential.

The SEM photographs for glass fiber surface morphology are shown in Fig. 2. Figure 2(a) shows that the glass fiber surface is smooth without the nano-silica treated with coupling agent. There are a lot of attachments when the glass fiber was pretreated with nano-silica and coupling agent (Fig.2(b)-(d)). The results show that the adhesion between the fiber and the nano-silica is improved when the nano-silica is pretreated with silane coupling agent.

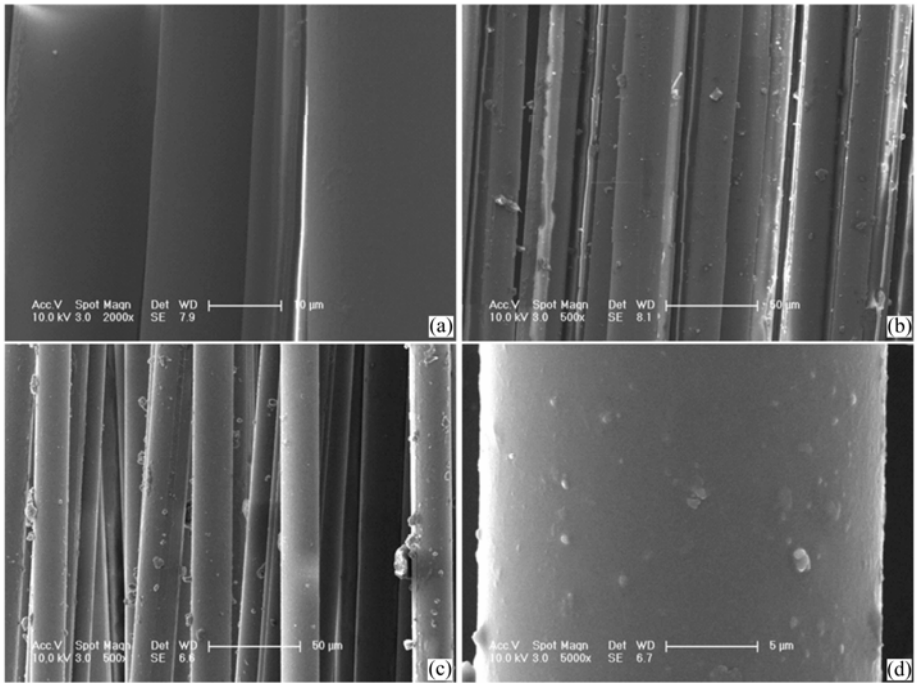

Fig. 2 SEM images for glass fiber surface morphology

(a) without nano-silica and coupling agent (2 000×); (b) glass fiber/nano-silica treated with KH550 (500×); (c) glassfiber/nano-silica treated with A-143 (500×); (d) glass fiber/nano-silica treated with A-151 (5 000×)

2.2 Effect of the Nano-Silica and Coupling Agent on the Composites Properties

It has been found that the storage modulus (E') of the composite increases with the addition of nano-silica treated with coupling agents (Figs. 3 and 4). Compared with the composites without the addition of the nano-silica and the coupling agent, the peak of the composite's loss factor (tan δ) value is shifting to higher temperature.

Interface cohesiveness (A) is according to Luis Ibrarra's formula[17]:

$$A = \frac{1}{1-V_f} \times \frac{\tan\delta_c}{\tan\delta_m} - 1$$

$\tan\delta_c$ and $\tan\delta_m$ are the loss factors for composite and matrix, respectively, V_f is the volume fraction of fiber. The smaller the value A, the stronger the interface cohesiveness. Ashida *et al*[18] proposed the following formula:

$$(\tan\delta_{max})_c = (\tan\delta_{max})_m - \alpha V_f$$

$(\tan\delta_{max})_c$ and $(\tan\delta_{max})_m$ are the maximum values of $\tan\delta$ for the composite and the matrix, respectively.

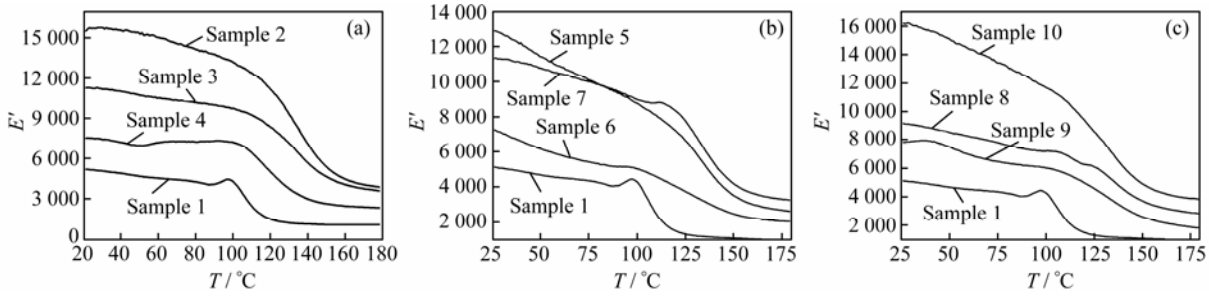

Fig. 3 Relationship between the composite storage modulus (E') and the dose of the silane coupling agent

(a) KH550; (b) A-143; (c) A-151

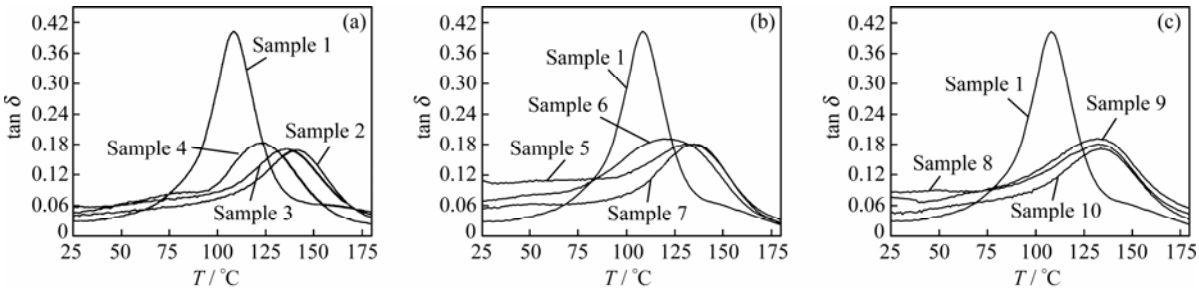

Fig. 4 Relationship between the loss factor (tanδ) and the dose of the silane coupling agent
(a) KH550; (b) A-143; (c) A-151

The parameter α is the characterization of the interfacial adhesion. It reveals that the relationship between the composite mechanical internal friction peak $(\tan\delta_{max})_c$, the pure basic internal friction peak $(\tan\delta_{max})_m$, and the interfacial bond strength. The greater the value α, the better the adhesion capacity of the interface. Table 2 shows that the $\tan\delta_{max}$ value of the glass fiber decrease with the addition of the treatment (nano-silica treated with the coupling agent). It indicates that the compatibility and the adhesion strength between the matrix and glass fiber increase with the addition of the assistant.

The three kinds of silane coupling agent have a better modification effect on improving the performance of the glass fiber/UPR composites. The composite materials all have good mechanical properties (as shown in Fig. 5).

Table 2 Glass fiber surface treatment methods on the material properties of the interface

Sample	$\tan\delta_{max}$	A	α
1	0.402 22	0.79	–0.136
2	0.168 75	–0.25	0.175
3	0.170 44	–0.24	0.173
4	0.182 33	–0.19	0.157
5	0.180 46	–0.20	0.159
6	0.190 97	–0.15	0.145
7	0.181 01	–0.19	0.159
8	0.180 43	–0.20	0.159
9	0.191 38	–0.15	0.145
10	0.171 44	–0.24	0.171

The storage modulus (E') of the composite is about 16 000 MPa with the 0.1% (m ∶ m) KH550 at room temperature**,** while the glass-transition temperature (T_g) also reaches up to be 140 ℃. When the dose of the KH550 increases to 0.25% (m ∶ m) and 0.5% (m ∶ m), the peak of the loss factor (tan δ) value has a little change; Meanwhile, E' and T_g value decrease significantly (as shown in Figs. 3-5). Fig. 5(a) shows that the impact strength of the composites is higher than that of the composite without the treatment. The impact strength is best when the dose of KH550 is 0.1% (m ∶ m). This result is as same as the DMA results.

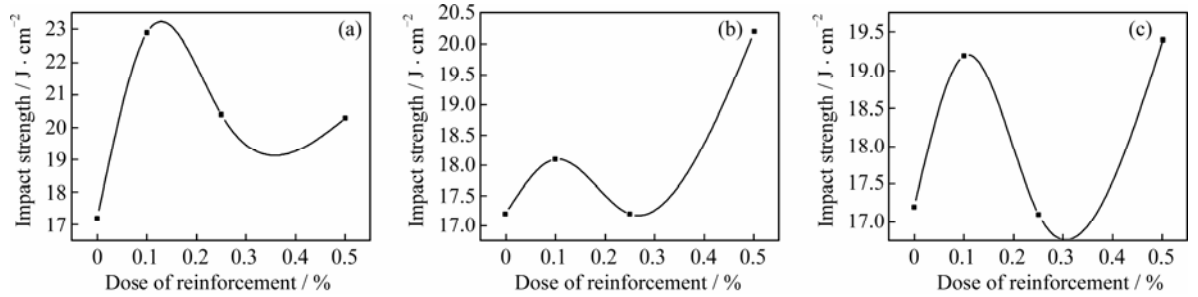

Fig. 5 Relationship between the composite impact strength and the dose of the silane coupling agent
(a) KH550; (b) A-143; (c) A-151

When the glass fiber is treated with A-143, the highest storage modulus of composite is 13 000 MPa (as shown in Fig.3(b)). The maximum impact strength is 19.4 J/cm^2 (as shown in Fig.5(b)). Moreover, the impact strength of the composite at the dose of 0.25% (m ∶ m) is the same as the nontreated one.

The storage modulus (E') of the composite treated with 0.5% (m ∶ m) A-151 reaches 16 000 MPa at room temperature, and T_g value also reaches up to 137 ℃ (as shown in Fig.4(c)). Figure 5(c) shows that the highest impact strength is 20.2 J/cm^2, which increases by 17.44%, as compared with the nontreated one.

It has been reported that there is no relationship

between the effect of the coupling agent on the polyester composite and the polarity of the organic functional groups of the coupling agent[9]. The glass fiber treated with chlorine propyl silane coupling agent has a very high surface energy. Therefore, the glass fiber can easily be infiltrated by resin solution. Vinyl in the vinyl silane coupling agent can react with the unsaturated bond of the UPR. The amino in the KH550 can react with the stem grafting anhydride functional groups and then enhance the interface bonding strength, thus further improving the performance of the composite. However, the three coupling agent can improve the dispersion effect of nano-silica. For this phenomenon, there are two reasons: 1) With the addition of coupling agent, the surface energy of nano-silica is lowered, the reunion of nano-silica in the matrix is decreased, and nano-silica can disperse easily. The surface energy of the polymer is low. Low surface energy of nano-silica can be more easily compatible with polymer matrix. 2) The surface of nano-silica treated with the coupling agent can form a soft interfacial layer. When the materials are subjected to stress, the layer can play a role as an inhibitor against crack growth. The kinetic energy and strain potential energy concentrated at the crack tip is converted into the non-continuity boundary deformation energy.

2.3 Glass Fiber/Unsaturated Polyester Resin Composites Fracture Morphology and Analysis

Through the observation of the SEM photograph of the fracture surface of the samples (as shown in Fig. 6), the effect of the surface treatment on the adhesion between glass fiber and the matrix and the relationship between the treatment and the performance is discussed.

Figure 6(a) shows that the fracture surface of the glass fiber is smooth when the glass fiber is not pretreated with silane coupling agent and nano-silica. SEM photographs of the fracture surface of the glass fiber treated with nano-silica (treated with 0.25% (*m* : *m*) KH550) /unsaturated polyester composites are shown in Fig.6 (b). It can be seen from the figure that the surface is not smooth and wrapped by the colloid layer. It explains that the combination of the fiber and the matrix is good. When the glass fiber is treated with A-143 and A-151 (as shown in Fig.6 (c) and (d)), the phenomenon of the glass fiber being pulled out do not exist.

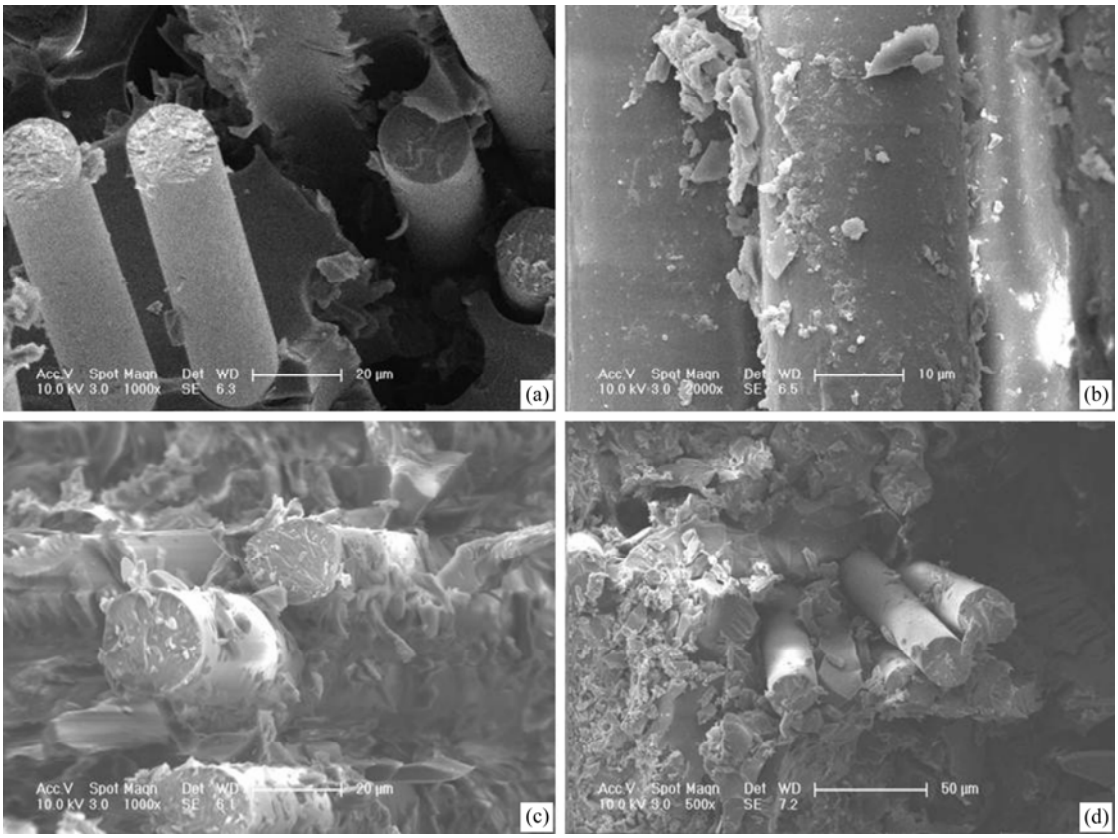

Fig. 6 SEM images of the fracture surface of the samples

(a) the untreated glass fiber composites (1 000×); (b) glass fiber treated with nano-silica /0.25%(*m*:*m*) KH550 (2 000×); (c) glass fiber treated with nano-silica /0.25% (m:m) A143 (1 000×); (d) glass fiber treated with nano-silica/0.25% (*m*:*m*) A151 (500×)

2.4 Enhanced Mechanism

The glass fiber and nano-silica can produce chemical reaction with the silane coupling agent. The silane coupling agents undergo hydrolysis reaction in the process of the treatment and then dehydrate to form the oligomer**,** which can form hydrogen bond with the hydroxyl group of the inorganic material surface, which further leads to dehydration reaction to form a covalent bond. Ultimately, the inorganic material surface has covered by the silane coupling agent (as shown in Fig. 7).

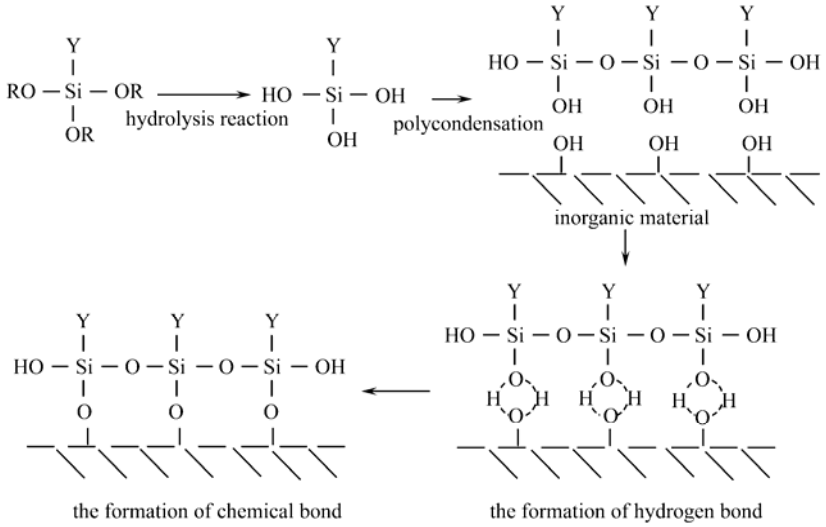

Fig. 7 The mechanism of the silane coupling agent and inorganic materials

Chemical bonding generate in the glass fiber's surface after the treatment of the silane coupling agent. The reactive functional group is a double bond and an amino group after the treatment of the A-151 and KH550. These groups can bond with the polyester resin matrix chemically or physically. Therefore, the interfacial bond strength of the fiber and the matrix material can be improved. The nano-silica treated with the coupling agent can improve the adsorption effect. Then, the substrate can bind more securely with the nano-silica, thereby improving the mechanical properties of the composite material.

3 Conclusions

1) According to the results of DMA and impact test, the samples modified with A-151 or KH550 show better performance. In addition, additive content (relative to the glass fiber) affects the mechanical properties of the material. Its performance is best when the glass fiber is treated with 0.1% (m∶m) KH550.

2) When the glass fiber is treated with nano-silica and silane coupling agents, the chemical bonds can be formed at the interface of the fiber and the matrix, which can improve the interfacial bond strength between the fiber and the matrix. Therefore, the mechanical properties of the materials are improved.

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