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Investigation of Properties of Nano-silica Modified Epoxy Resin Films and Composites using RFI Technology

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Abstract

The carbon-fiber-reinforced composites modified by nano-silica were successfully prepared using RFI technology. And the properties of composites also were studied. The investigations revealed that the properties of composites were increased by filling nano-silica. With the increase of nano-silica content, the density of carbon-fiber-reinforced composites was increased, while the glass transition temperature, tensile strength and flexural strength were first increased and then decreased. At the nano-silica content of 3wt%, the glass transition temperature reached a maximum of 117.3℃. When the nano-silica content was 4wt%, the tensile strength and flexural strength were increased to 595.69 and 703.76 MPa, which were improved by 86.30% and 126.98% compared with the composites without nano-silica. Therefore, the best properties of carbon-fiber-reinforced composites was obtained with filling 4wt% nano-silica content, while the toughening and strengthening effect was optimal, since nano-silica as a reinforced material were filled the gap between epoxy resin and carbon fiber to disperse the external force.

Keywords:
A. Polymer-matrix composites (PMCs);
B. Properties;
E. RFI technology.

1. Introduction

Composites, which are made of two or more materials, have not only properties of the original single material, but also that of excellent mechanical properties and thermal stability because of the synergistic effect among the components. Epoxy resins are widely being used as matrix materials due to highly cross linked structure, which bring a remarkable improvement in some properties of epoxy composites [1-8]. However, there are limitations to prepare epoxy composites because of low toughness caused by its highly cross linked structure. To overcome the disadvantage, some nanoparticles were added to matrix. In recent years, inorganic particles have been extensively applied to prepared organic/inorganic composites, which have significantly improved the related properties of composites materials [9-16]. For example, filling nano-silica into organic polymer could combine the characteristics of nano-silica such as rigidity, thermal stability and so on with the properties of organic polymer, thus preparing composites with excellent mechanical properties and thermal stability [17-23].Hence adding inorganic particles into epoxy resin to prepare organic/inorganic composites has become an important way to develop high-performance functional materials [24-26].

In this paper, modified epoxy resin films and composites were prepared by advanced liquid composite molding technology-resin film infusion (RFI) process. In the process of preparing composites, the inorganic nanoparticles were filled and distributed well in the resin, then gradually permeated with the resin along the thickness direction of fiber under the action of negative pressure, and finally passed through the carbon fiber cloth, thus preparing special functional materials made of organic polymer and fiber. Meanwhile, the changing tendency of performance of the resin films and composites modified by nano-silica using RFI technology were researched by the analysis and test of properties of the resin film and composites.

2. Experimental

2.1 Materials

Epoxy resin LY1564 with viscosity range from 1200 to 1400 mPa·s at T = 25℃ was supplied by Huntsman Advanced Materials LLC., America. Nano-silica with an average diameter of 15 nm and boron trifluoride ethylamine complex were purchased from Aladdin Industrial Co., China. Absolute ethanol and ethylene glycol were provided by Sinopharm Chemical Reagent Co., Ltd., China. Silane coupling agent KH550 was obtained from Hubei Novel organic silicon materials Co., Ltd. of Wuhan University, China. Additionally, all reagents were used without further purification. Carbon fiber plain woven fabrics was prepared by Wuxi Weisheng Composite Materials Co., Ltd., China, which had a thickness of 0.2 mm. High vacuum silicone grease GZ-I was provided by Tongxin chemical plant in Caidian District of Wuhan, China.

2.2 Preparation

2.2.1 Preparation of Nano-silica Modified Epoxy Resin Films using RFI technology

The preparation of nano-silica modified epoxy resin films followed the procedure as follows. Silane coupling agent KH550 and nano-silica were mixed and reacted in ethanol solution under continuous stirring and ultrasonic treatment. And then the mixture solution was dialysed by high-speed centrifuge to obtained pretreated nano-silica. The surface-treated nano-silica was synthesised by stoving and grinding. The boron trifluoride ethylamine complex was dissolved in ethylene glycol according to corporate formula. Epoxy resin LY1564 was added into the solution under continuous stirring and ultrasonic treatment. After reaction for 2 h, the previously prepared surface-treated nano-silica was added into solution. The mixtures were stirred for another 1 h, and finally the nano-silica modified epoxy resin films were prepared through the steps of thermal stirring and coating films.

2.2.2 Preparation of Nano-silica Modified Epoxy Resin Composites using RFI technology

The preparation process of epoxy resin composites was shown in figure 1. The mould filling with materials was putted into the vacuum bag and placed on the vulcanizing press to heat, thus contributing to solidification and formation of the epoxy resin composites. A closed vacuum environment was formed by the use of vacuum pump, air hose, storage bottle of abandoned resin and vacuum bag, which was good for eliminating air bubbles to prepare epoxy resin composites with the advantage of less cavity and smooth surface. The gas in the materials was extracted from the air hose by vacuum pump, so as to eliminate the bubbles, and then the epoxy resin composites with few cavities and smooth surface was prepared successfully. The storage bottle of abandoned resin was used to prevent the abandoned resin from entering the vacuum pump directly between the vulcanizing press and the vacuum pump.

3. Results and discussion

3.1 Effect of Nano-silica on viscosity of epoxy resin

In order to ensure that the fiber reinforcement was fully infiltrated with the resin matrix, the epoxy resin films used in RFI process require a low viscosity at operating temperature [27-29], so that the low viscosity is one of the key conditions for the molding process [30-33]. By measurements of the viscosity curve of the epoxy resin mixture and the epoxy resin film, it can determine whether the resin film is prepared by using resin mixture via the techniques of prepolymerization at a certain temperature satisfy the process requirements, thereby determining the optimal preparation parameters of the resin film. Fig. 2. and fig. 3 show the kinematic viscosity curve of epoxy resin mixture and resin film modified by different content of nano-silica at different temperatures. The initial viscosity increases with the increase of nano-silica content. When the nano-silica content was 5wt%, the viscosity of the resin system was very high due to the large specific surface area of nano-silica so that the resin mixture could not be stirred at room temperature. Even the viscosity of the resin system was 8600 mPa•s at 80℃. First, as the temperature increased, the viscosity of the resin system decreased sharply. The minimal viscosity ranged from 48.9 to 562 mPa•s at 110℃. Then the viscosity of the resin system rose slowly with the temperature increased. When the temperature reached to 120℃ the viscosity of the resin system increased significantly because of the decomposition of boron trifluoride ethylamine complex. Above 120℃, the viscosity of the resin system rose due to curing, in which the viscosity of the pure resin system varied greatly. In particular, the pure epoxy resin system prepolymerized to 120℃ will cured in 10 min if the heating is stopped.

3.2 Effect of nano-silica on gel time

Fig. 4 displays the relationship between the gel time of the epoxy resin film and the temperature. As the temperature increased, the gel time of the epoxy resin film was gradually shortened. However, In the process of preparing the epoxy resin film, sufficient time to infiltrate and fill is the key of preparation of the epoxy resin film for preventing curing in advance during the process of filling. For pure resin system, the infiltration temperature was 110-130℃ to ensure that the resin filling time was greater than 30 min (fig. 2 and 3). With the addition of nano-silica, the gel time was gradually shortened. When the content of nano-silica reached 5 wt%, the gel time was 100 min at 100℃, compared with only 35 min at 110℃. Thus, the optimal infiltration temperature of 110℃ was confirmed considering the gel time of nano-silica modified resin film. At this temperature, it was ensured that the resin film was prepared with sufficient time for filling to ensure that the resin was infiltrated enough with the reinforcing fibers in the RFI molding process, thereby making the nano-reinforcing material fully in contact with the reinforcing fibers.

Due to the good thermal properties of nano-silica [17], the rising trend of viscosity of the resin added with nano-silica was more obvious than that of the pure resin at 120 ℃. When the prepolymerization temperature was up to 120℃, if the heating was stopped, the curing reaction of the resin system added nano-silica did not occur vigorously. The gel time of prepolymerization temperature was 40 min, which provided sufficient time to ensure that the film was prepared succesfully. So the reaction rate of LY1564 epoxy resin with a long gel time could be reduced by adding nano-silica.

3.3 Effect of nano-silica content on glass transition temperature

The glass transition temperature (T_g) reflects the thermotolerance of the cured resin [34-36]. In this paper, the glass transition temperature of resin cast with different nano-silica content was determined using thermo-mechanical method by measuring the change of loss factor tanδ relative to temperature. The figure 5 shows the DMA curve of resin cast with different nano-silica content.

The temperature corresponding to tanδ peak is commonly taken as glass transition temperature. The T_g of epoxy resin system was obviously increased after adding nano-silica shown in Fig. 5. When nano-silica content was up to 1 wt%, the T_g value of pure epoxy resin changed from 83.7℃ to 101.3℃. With the increase of nano-silica content, the T_g of resin cast increased first and then decreased slightly. When the content of nano-silica was up to 3 wt%, the T_g value rised to 117.3℃, which was 33.6 ℃ larger than that of pure resin cast.

The thermotolerance of the cured resin was increased to a certain extent due to the strong interaction between epoxy resin and nano-silica particles by adding nano-silica. As the nanoparticles undergo a surface treatment with a silane coupling agent, the coupling agent on the surface of nanoparticles acted as a crosslinking point in the matrix was easily twined with the epoxy resin chain, resulting in physical crosslinking. And these coupling agents were bonded with the matrix, so that a good interface effect was formed between epoxy resin and nano-silica particles. Therefore, the introduction of nanoparticles was conducive to improving the T_g of epoxy resin system.

3.4 Influence of nano-silica content on fiber volume content and density of carbon-fiber-reinforced composites

The density of the carbon-fiber-reinforced composites prepared by adding nano-silica into the epoxy resin varied with the content of nano-silica is shown in Table 1. With the addition of nano-silica content, the density of the carbon-fiber-reinforced composites increased, whose values were 1.35-1.67 g/cm^3.

The main advantage of the carbon-fiber-reinforced composites prepared by nano-silica modifying epoxy resin films using RFI technology is high fiber volume content [37, 38], which also is an important parameter to characterize infiltration effect and material properties of the resin and fiber. The dependence of the fiber volume content on the nano-silica content is shown in Table 2, which was obtained by the method of burning-loss and separation. From the table 2, the fiber volume content was remained about 58% and much higher than that of the carbon-fiber-reinforced composites prepared by traditional process. Due to the addition of the filler, the density of the carbon-fiber-reinforced composites was increased, but the arrangement of the fibers was unchanged. The nano-silica molecules were filled in the voids between fibers and resin, which did not change the total content of the fibers, so the volume content of the fibers was constant even when the nano-silica content increased.

3.5 Influence of nano-silica on porosity of carbon-fiber-reinforced composites

Another advantage of carbon-fiber-reinforced composites is Low porosity [39, 40]. As an important parameter of carbon-fiber-reinforced composites, porosity was used to characterize infiltration effect of the resin and fiber by microscopic labeling method. The surface morphology of carbon-fiber-reinforced composites modified by nano-silica with different contents and the relationship of porosity and nano-silica content were displayed as Fig. 6 and Table 3, respectively. The porosity of the carbon-fiber-reinforced composites was significantly decreased after the filling of nano-silica, because nano-silica penetrated along the thickness of the composites as the resin flow in RFI process and sufficient contact with resin and fibers to fill the gap of fibers in the infiltration process and voids produced during the resin curing process, thus blocking the flow of nano-silica and suppressing the shrinkage of the matrix by vacuum to reduce the porosity of the carbon-fiber-reinforced composites. Hence porosity of the carbon-fiber-reinforced composites was reduced via filling nano-silica.

3.6 Influence of nano-silica on the permeability of carbon fiber cloth

The distribution of the particles in the carbon fiber cloth directly affects the properties of the carbon-fiber-reinforced composites [41, 42], which also contributes to study of filling of functional particle in the future [43]. In this paper, the epoxy resin film modified by nano-silica was used in RFI process to prepared carbon-fiber-reinforced composites. In order to research the permeability of the nano-silica particles in the course of RFI, the composition of surface and along the thickness direction of carbon-fiber-reinforced composites was analyzed by electron spectroscopy analysis (EDS). The distribution of particles in the thickness direction of the carbon-fiber-reinforced composite and the permeability of the surface are shown in Figures 7 to 12.

The plane scans of element are shown in Figure 7-12. The thickness direction of carbon-fiber-reinforced composite laminates is rich in C, O and Si. Fig. 7 shows the element distribution in the thickness direction of the carbon-fiber-reinforced composite laminates without nano-silica. Compared with Fig. 8, the Si elements were homogeneously distributed in in the thickness direction of the carbon-fiber-reinforced composite laminates. Along the flow direction of the resin, the region with more C elements was the distribution area of the carbon fibers. And the Si element distribution at the intensive region of fiber was decreased than other regions, so the 20 layers of carbon fiber had played a blocking role in nano-silica flowing with resin. But overall Si element was distributed evenly in the thickness of carbon-fiber-reinforced composite laminates. However, the Si elements aggregation was observed in the particular region of carbon-fiber-reinforced composite laminates when nano-silica flowed through the region with resin. In Fig. 9, the nano-silica distributed uniformly in the thickness direction of the composite laminates using 40 layers of carbon fiber cloth. And darkest regions were observed, because the existence of carbon fiber in this area caused uneven surface of the composite laminates. By zoom spectrum, the evenly distribution of the nano-silica was observed in the carbon-fiber-reinforced composite laminates. In summary, the uniform distribution of the nano-silica is very important for the performance of the composites, indicating that the nano-particles fillng in RFI process contributes to prepare the carbon-fiber-reinforced composites.

Fig. 10 displays the plane scan of nano-silica modified carbon-fiber-reinforced composite laminate surface. The surface is the end of the resin infiltration. Since the process requirement of preparing the carbon-fiber-reinforced composite laminates, the release cloth and ventilated felt are used, resulting in the filling particles agglomeration in the surface. Hence, the permeability of the nanoparticles in the carbon-fiber cloth was explained by studying the distribution of Si element in surface. In Fig. 11, the C and O elements were uniform distributed in the surface of the composite laminates prepared by the 20 layers carbon fiber cloth. The Si element distribution in the surface was less than that in the thickness direction of composite laminates, because nano-silica easily was absorbed to the release cloth and ventilated felt under vacuum pressure, so the region with less Si element distribution was that with high vacuum pressure. Fig. 12 shows the similar Si elements distribution in surface of composite laminates made by the 40 layers carbon fiber cloth with Fig. 11. Si elements agglomeration also were observed in surface of carbon-fiber-reinforced composite laminates. Comparison with the thickness direction of composite laminates, the distribution of nano-silica in carbon fiber was relatively uniform. And the Si elemental distribution in the surface showed that the nano-silica could travel to surface from the bottom of carbon fiber cloth by infiltration. Hence it is found that the inorganic/organic carbon-fiber-reinforced composites were prepared using RFI technology that made the resin film modified by nano-silica particles well penetrated the carbon fiber materials by the plane scan of EDS analysis.

3.7 Effect of nano-silica on the mechanical properties of carbon-fiber-reinforced composites

The tensile and bending properties of the composite laminates prepared by the 20 layers carbon fiber cloth using RFI technology were displayed in Fig. 13. As nano-silica content increased to 1wt%, the tensile and bending strengths were greatly improved. The tensile and bending strengths of composite laminates were increased by 23.56% and 75.26%, respectively. The tensile strength was changed from 319.75 to 395.09 MPa and the bending strength was improved from 310.05 to 543.39 MPa when the nano-silica content changed from 0 to 1wt%. With the further increase of nano-silica content, the tensile and bending strengths of composite laminates was increased. The values of maximum tensile strength and bending strength obtained when nano-silica was filled about 4wt% were 595.69 and 703.76MPa, which increased by 86.30% and 126.98% compared with pure epoxy resin, respectively. As nano-silica content further increase to 5wt%, the tensile and bending strengths was decreased due to the strong blocking effect caused by agglomeration of carbon fiber in RFI process resulting stress concentration.

3.8 Effect of nano-silica on the microstructure of carbon-fiber-reinforced composites

In the mechanical experiment of carbon-fiber-reinforced composites, the tensile fracture surface morphology of was characterized by using the scanning electron microscope (SEM), as shown in Figure 14-16.

Fig. 14 shows the SEM images of carbon-fiber-reinforced composites without nano-silica. In Fig. 15. (a), the bright white spot was observed in surface of composites because of adding 2wt% nano-silica, indicating the nano-silica particles aggregated at the bright white spot. Comparing the three images (b), microcracks were produced in the matrix of the resin as the nano-silica filling. With the nano-silica content increasing, the number of microcracks was increased leading to large surface roughness. The mechanical properties of composite laminates added with nano-silica were increased by two reasons. First, nano-silica had played function of reinforcing and toughening when nano-silica was filled in the resin matrix. Second, nano-silica was adsorbed on the surface of carbon fiber in RFI process to fill the gap between carbon fiber and resin, thus the stress caused by external force was dispersed to achieve reinforcing and toughening effect.

4. Conclusions

The inorganic particles modified composites were successfully prepared via filling inorganic particles into epoxy resin films and using RFI technology and the properties also were studied. It was shown that the viscosity of epoxy resin mixtures was increased and the curing reaction of the epoxy resin system was significantly reduced when nano-silica was filled, indicating the gel time could be increased to 40 min while the formation process of resin films was not affected by controlling nano-silica content. The glass transition temperature was increased at first and then decreased with the increasing content of nano-silica, the maximum values of glass transition temperature of cured resin was 117.3℃ when nano-silica content was 3wt%. And the density of carbon-fiber-reinforced composites was improved as the increasing nano-silica content. EDS analysis showed the permeability of composites made by 20 or 40 layers carbon fiber was good. Si element was uniformly distributed in the entire plane and no obvious aggregation of element was found in the side and surface of composites. Analyzed the mechanical properties of carbon-fiber-reinforced composites modified by different nano-silica content, the tensile strength and flexural strength were increased by filling nano-silica. When nano-silica content was increased to 4wt%, the maximum values of tensile strength and flexural strength were obtained and improved by 86.30% and 126.98% than that of composites without nano-silica, which were 595.69 and 703.76 MPa. In SEM micrographs, it was found that excellent toughening and strengthening effects of carbon-fiber-reinforced composites were achieved with filling 4wt% nano-silica. As the nano-silica fill the gap between resin and carbon fiber, the resin and the fiber surface were completely in contact with each other to disperse the external force so as to enhance toughening and strengthening effect.

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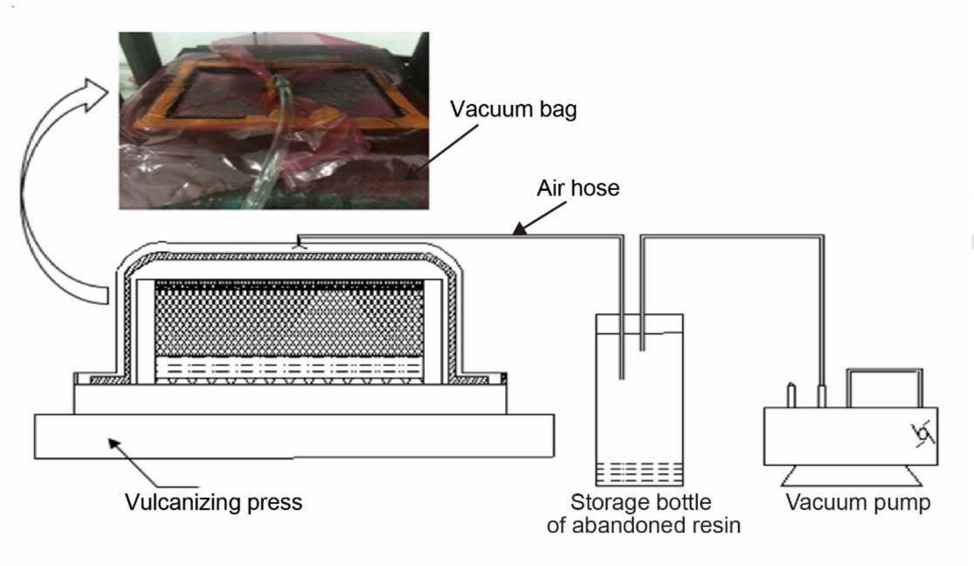

Fig. 1. Process flow diagram of nano-silica modified epoxy resin composites using RFI technology

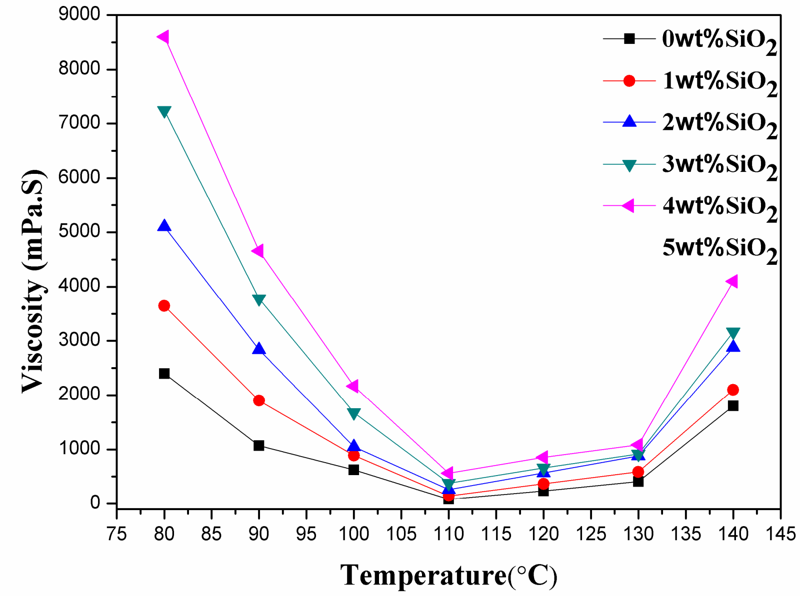

Fig.2. Kinematic viscosity curve of epoxy resin mixture modified by different content of nano-silica at different temperatures

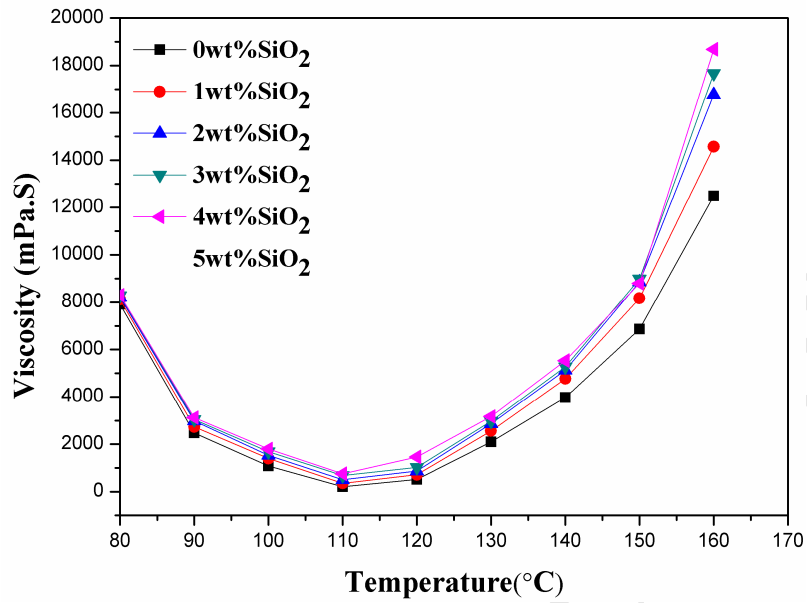

Fig.3. Kinematic viscosity curve of resin film modified by different content of nano-silica at different temperatures

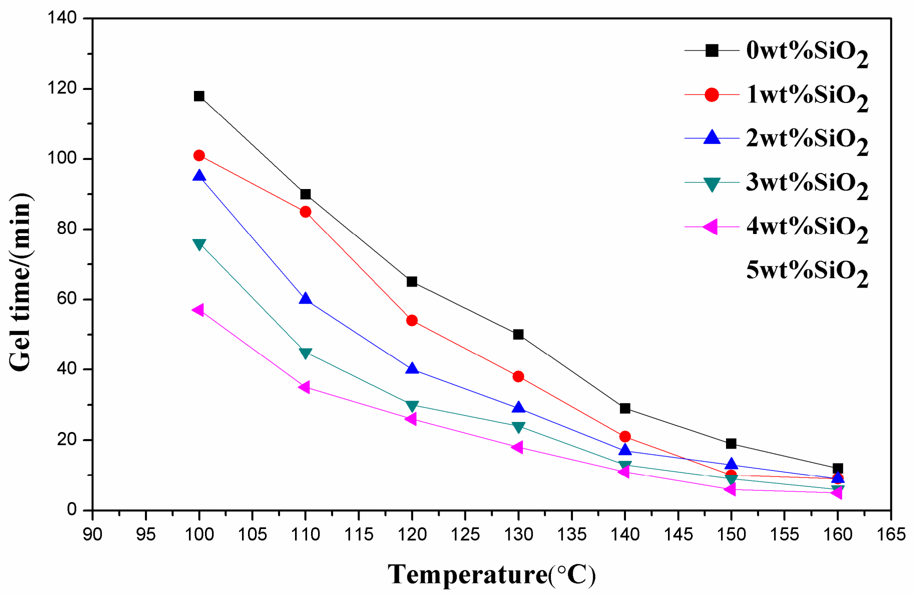

Fig. 4. The gel time curve of the resin film at different temperatures

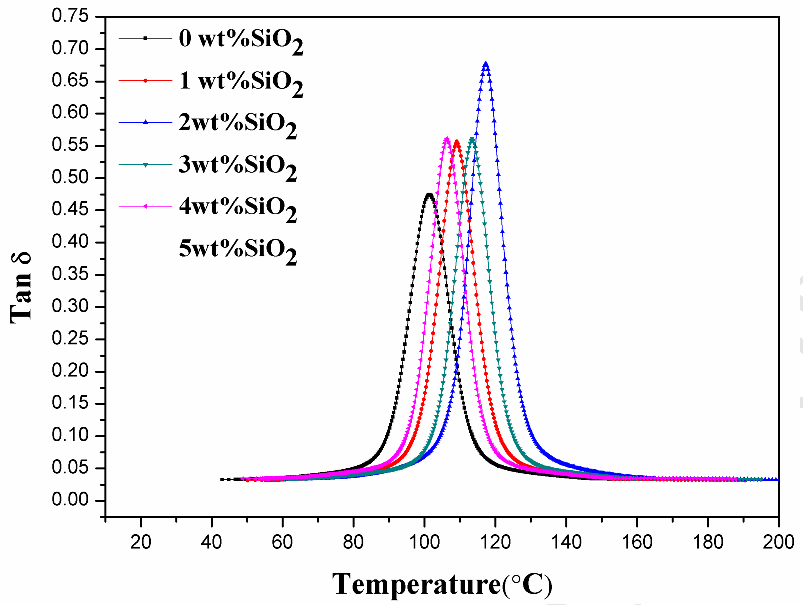

Fig. 5. DMA curve of resin cast with different nano-silica content

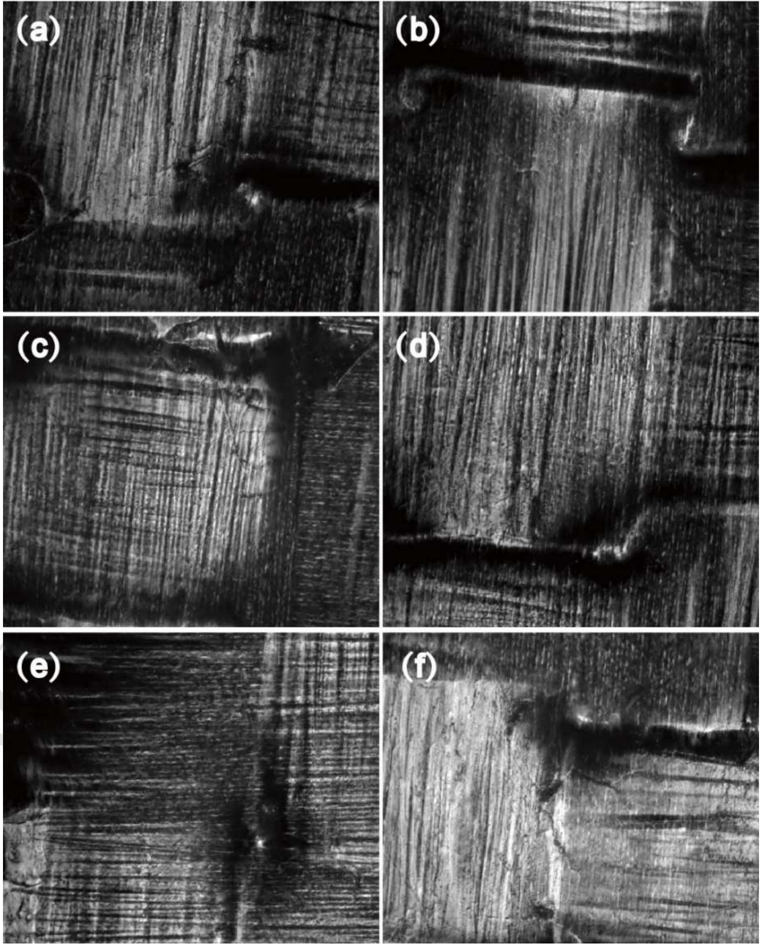

Fig. 6. SEM images of carbon-fiber-reinforced epoxy resin modified by nano-silica with different contents (a) 0 wt%, (b) 1 wt%, (c) 2wt%, (d) 3wt%, (e) 4wt%, (f) 5wt%

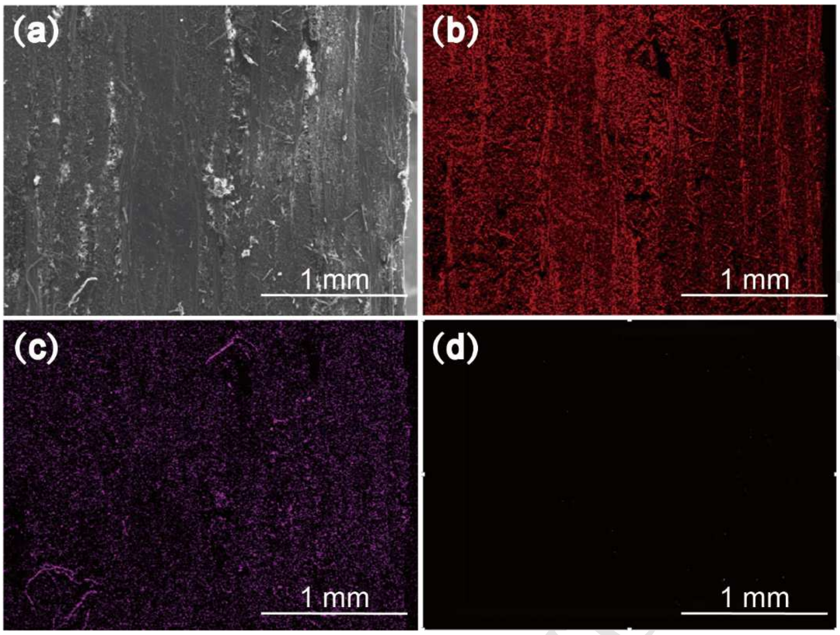

Fig. 7. SEM and EDS element images of carbon-fiber-reinforced epoxy resin without nano-silica in in the thickness direction (40 layers) (a) cross-sectional SEM image, (b) EDS image of C element, (c) EDS image of O element, (d) EDS image of Si element

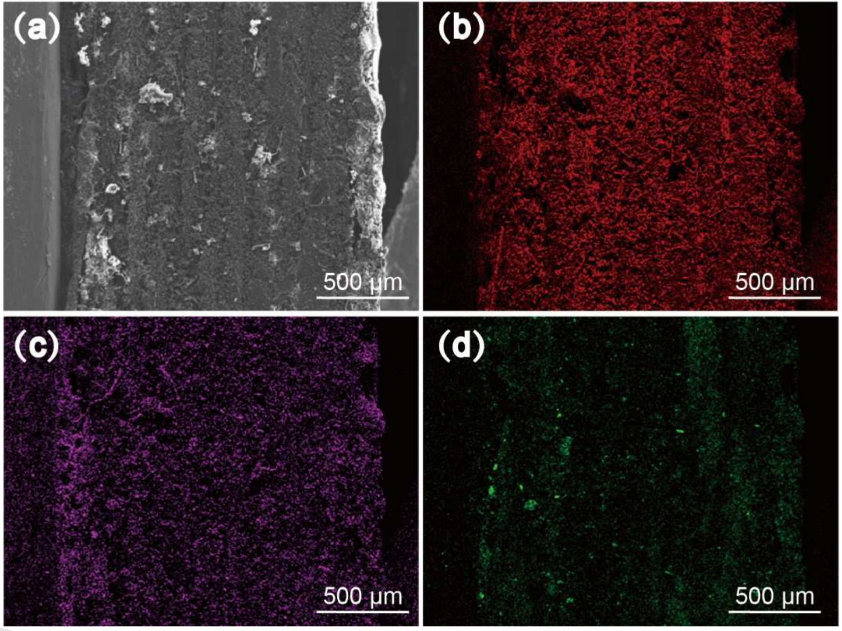

Fig. 8. SEM and EDS element images of 4wt% nano-silica modified carbon-fiber-reinforced epoxy resin in the thickness direction (20 layers) (a) cross-sectional SEM image, (b) EDS image of C element, (c) EDS image of O element, (d) EDS image of Si element

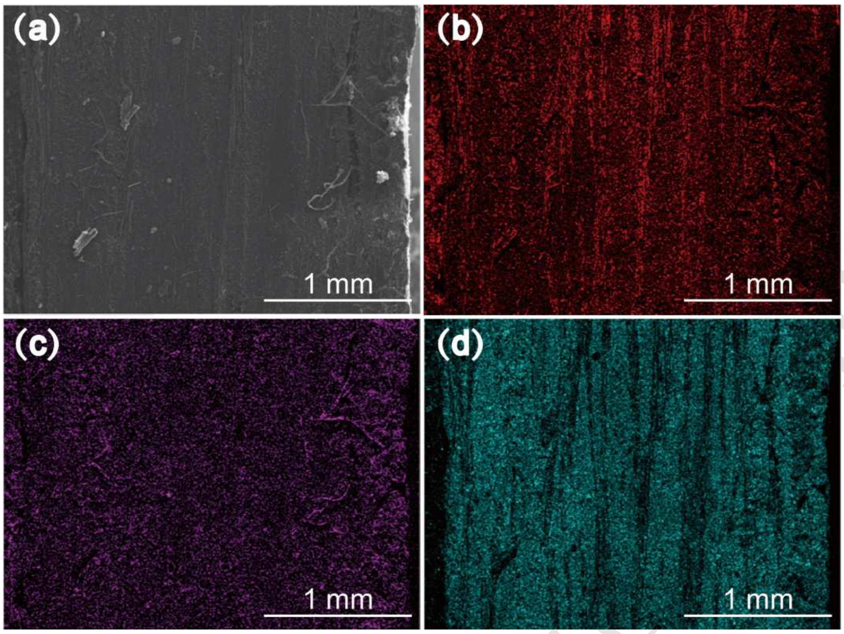

Fig. 9. SEM and EDS element images of 4wt% nano-silica modified carbon-fiber-reinforced epoxy resin in the thickness direction(40 layers) (a) cross-sectional SEM image, (b) EDS image of C element, (c) EDS image of O element, (d) EDS image of Si element

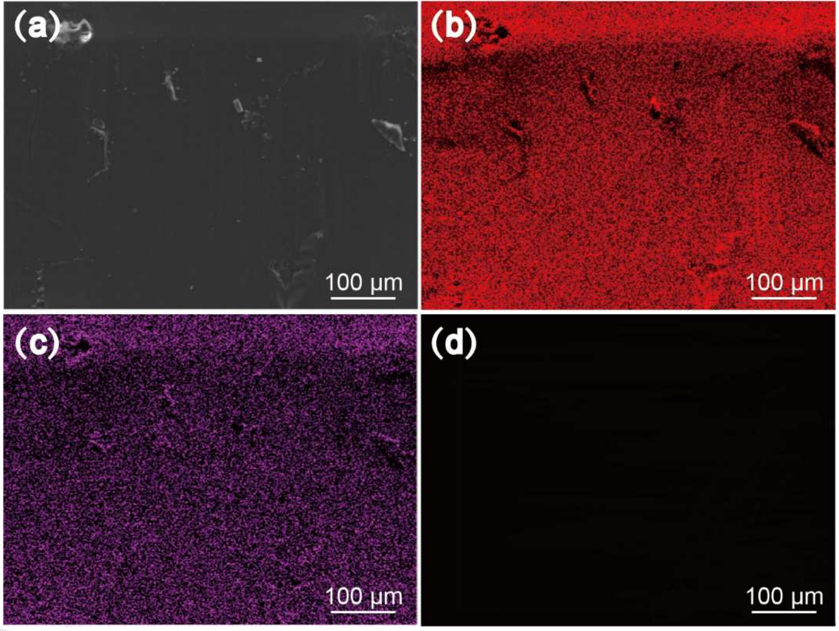

Fig. 10. SEM and EDS element images of carbon-fiber-reinforced epoxy resin without nano-silica in surface (40 layers) (a) surface SEM image, (b) EDS image of C element, (c) EDS image of O element, (d) EDS image of Si element

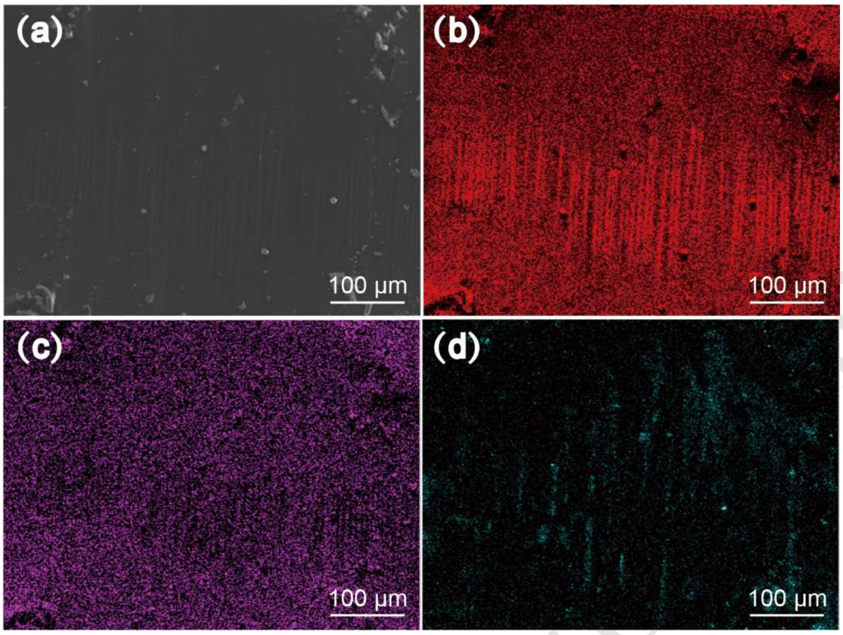

Fig. 11. SEM and EDS element images of 4wt% nano-silica modified carbon-fiber-reinforced epoxy resin in surface (20 layers) (a) surface SEM image, (b) EDS image of C element, (c) EDS image of O element, (d) EDS image of Si element

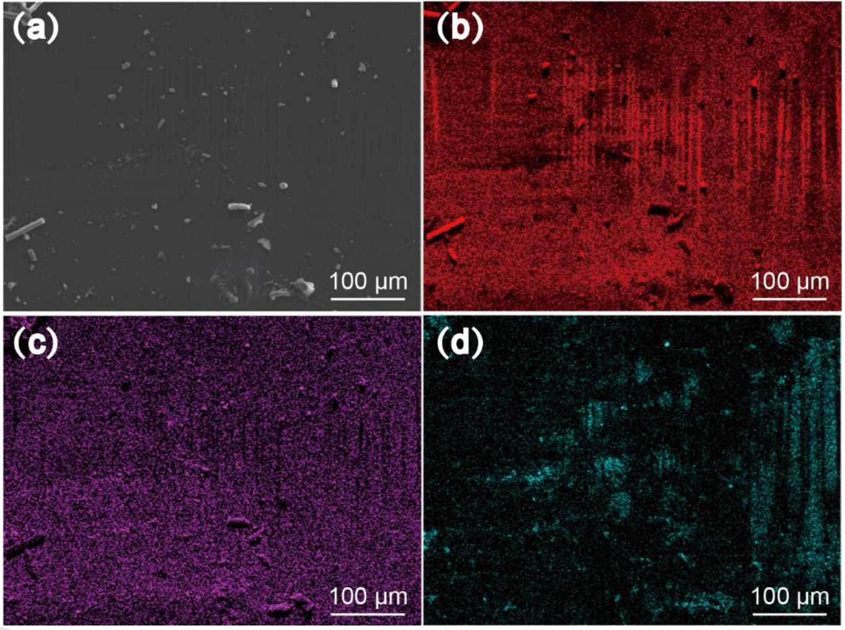

Fig. 12. SEM and EDS element images of 4wt% nano-silica modified carbon-fiber-reinforced epoxy resin in surface (40 layers) (a) surface SEM image, (b) EDS image of C element, (c) EDS image of O element, (d) EDS image of Si element

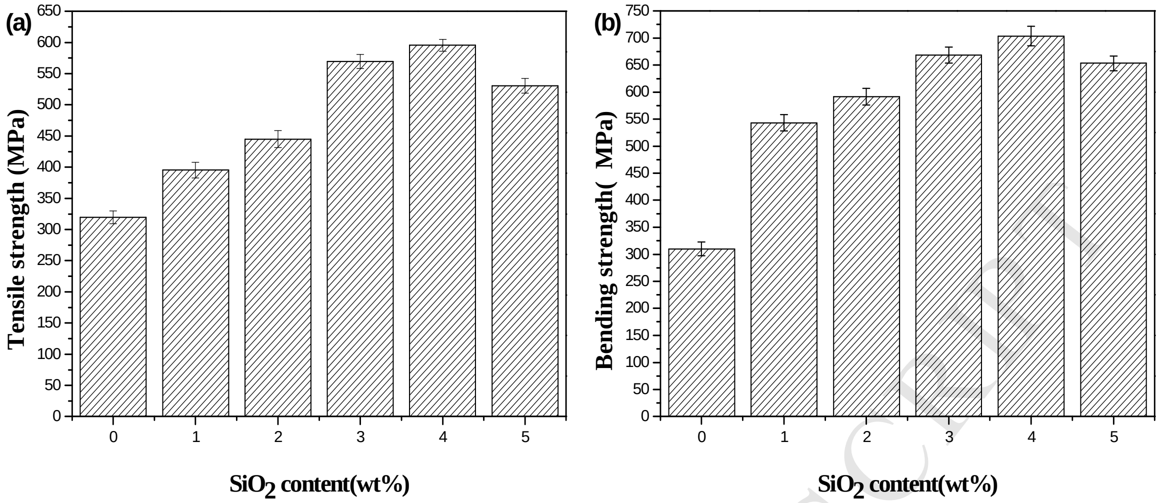

Fig. 13. Variety of (a) tensile and (b) bending strengths of carbon-fiber-reinforced composites with nano-silica content

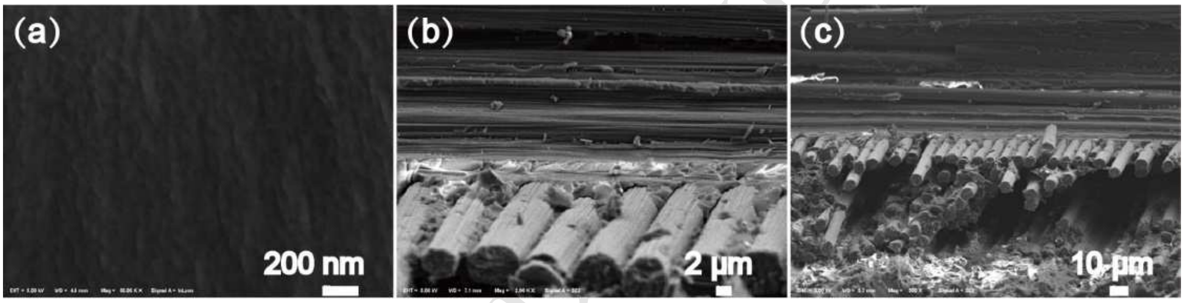

Fig. 14. SEM images of carbon-fiber-reinforced composites without nano-silica

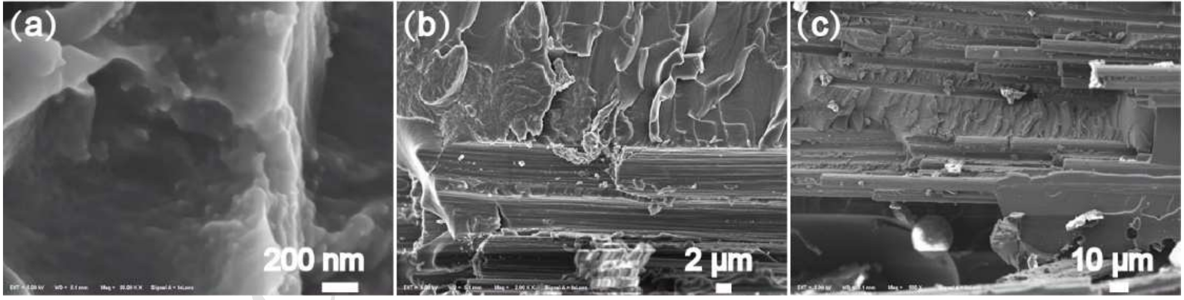

Fig. 15. SEM images of carbon-fiber-reinforced composites modified by 2wt% nano-silica

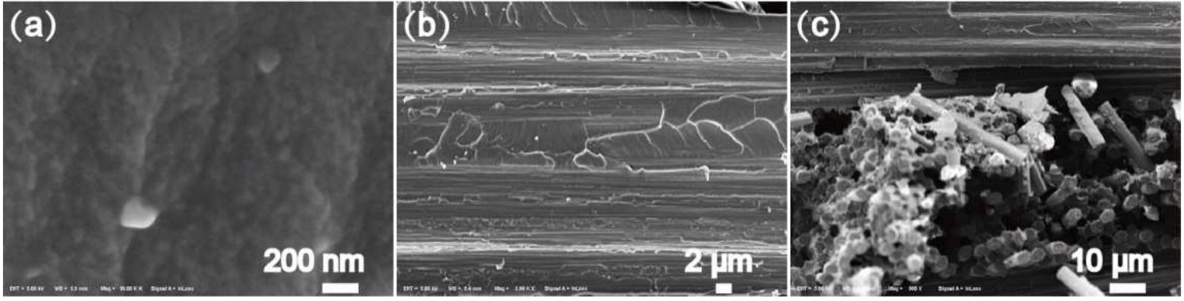

Fig. 16. SEM images of carbon-fiber-reinforced composites modified by 4wt% nano-silica

Table 1 Changes in density of nano-silica modified carbon-fiber-reinforced epoxy resin with nano-silica content

Sample	Density(g/cm^3)
0wt% nano-silica	1.35
1wt% nano-silica	1.57
2wt% nano-silica	1.59
3wt% nano-silica	1.60
4wt% nano-silica	1.63
5wt% nano-silica	1.67

Table 2 Dependence of the nano-silica content on the fiber volume content of nano-silica modified carbon-fiber-reinforced epoxy resin

Sample	Fiber volume content（%）
0wt% nano-silica	58.65%
1wt% nano-silica	57.99%
2wt% nano-silica	58.23%
3wt% nano-silica	58.14%
4wt% nano-silica	58.76%
5wt% nano-silica	58.68%

Table 3 Variation of porosity of nano-silica modified carbon-fiber-reinforced composites with nano-silica content

Sample	Porosity (%)
0wt% nano-silica	3.26
1wt% nano-silica	2.07
2wt% nano-silica	1.57
3wt% nano-silica	1.23
4wt% nano-silica	1.09
5wt% nano-silica	0.97