

Research Article

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Nano-silica modified phenolic resin film: manufacturing and properties

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Abstract: Nano-silica modified phenolic resin film is prepared using different mass fractions of nano-silica by liquid composites molding (LCM). The effects of nano-silica on the rheology and curing of phenolic resin are studied by rheometer and differential scanning calorimeter (DSC). The results show that the viscosity of nano-silica modified phenolic resin decreases with the increase of temperature, and the viscosity is lowest between 70°C and 90°C. The appropriate resin film infusion (RFI) process is investigated, and the stepped curing process system is established. In addition, the microstructures of modified phenolic film and composites are tested by scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). Nano-silica can be uniformly dispersed in phenolic resin when the amount of nano-silica added is $\leq 4\%$. And the mechanical properties of nano-silica modified phenolic composites are tested by universal material testing machine. The optimum nano-silica mass loading for the improvement of mechanical properties is found. This work provides an effective way to prepare the modified phenolic resin film suitable for resin film infusion (RFI) processes, and it maybe become a backbone of thermal protection material in aerospace.

Keywords: nano-silica; phenolic resin; resin film infusion

1 Introduction

The properties of resin matrix have a great influence on the properties of composite material [1]. In many engineer-

ing applications, the performance of phenolic resin does not replace epoxy resin and polyimide resin, but phenolic resin still has special value in many aspects. Due to its chemical structure and cross-linking structure, phenolic resin has excellent flame retardant performance and high temperature resistance [2, 3]. It can be widely used in adhesives and insulating materials [4–6]. And phenolic resin-based composite materials have the advantages of low cost, good heat resistance, flame retardancy, and corrosion resistance, which can be widely used as thermal protection materials in the aerospace field, especially used in key components such as the expansion section of rocket engine nozzle [7–12].

In recent years, nanoparticles reinforced resin coatings have drawn a considerable attention, caused by the improvements on various properties, such as rheological properties, curing performance, heat stability and other mechanical properties [13, 14]. The use of inorganic particles in the nano scale range is particularly attractive, since it improves the properties of the polymers by controlling the degree of interaction between the polymer and the nanoparticles via a top-down approach [15]. Due to the unique surface and volume effects of nanoparticles, the performance of modified phenolic resin will be greatly improved [16–19]. Moreover, the surface of the nanoparticles has unpaired atoms, which can be physically or chemically bonded to the phenolic resin to enhance the interface with the matrix, thereby the performance of phenolic resin has been improved [20–24]. By the introduction of nanoparticles, the mechanical properties of phenolic resin can be significantly improved [25–27].

To the best of our knowledge, few works have been conducted on the manufacture and properties of phenolic resin film modified by nanoparticles. It is necessary to study nanoparticles modified phenolic resin film on the microscale and nanoscale.

In this paper, the effects of introducing nano-silica particles on the rheological properties and curing properties of phenolic resin film are investigated. By comparison in the rheological properties and curing properties of phenolic resin film, the optimum mass fraction of introduced nano-silica particles could be found. Finally, the dis-

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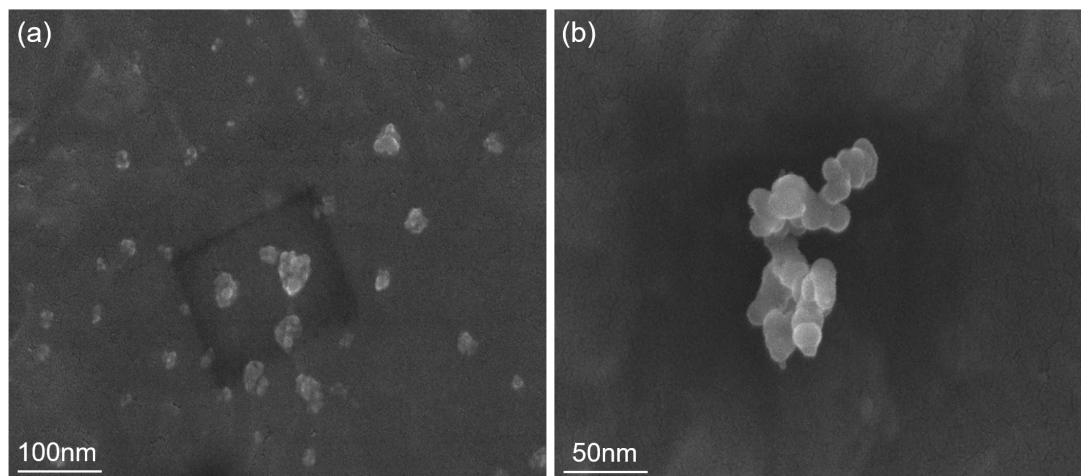


Figure 1: (a) High magnification SEM image of nano-silica; (b) Details of (a)

tribution of nano-silica particles on the surface of composites and the mechanical properties of nano-silica modified phenolic composites are characterized by scanning electron microscope and universal material testing machine in order to understand each mechanism operating during the resin film infusion (RFI) process.

2 Experimental procedures

2.1 Materials

B80 phenolic resin (brown viscous liquid) is purchased from Handan City Tianyu High Temperature Resin Materials Co., Ltd and used as received. Nano-silica particles (purity >95%) is supplied by Shanghai Aladdin Biochemical Technology Co., Ltd. The nanoparticles are modified by the coupling agent, and followed by the mechanical stirring, so that the nanoparticles can be well dispersed. As shown in Figure 1, nano-silica particles are dispersed homogeneously, and the distribution of particle size is 10–30 nm. Quartz fiber cloth (thickness of 0.2 mm, grams per square meter of 150 gsm) is supplied by Hubei Feilihua Quartz Glass Co., Ltd and used as received.

2.2 Sample preparation

A certain amount of phenolic resin is treated as 100 parts, and 0, 2, 4 and 6 parts of nano-silica are introduced respectively. The preparation of resin film is as follows. First, B80 phenolic resin and nano-silica particles are placed in an oven at 80°C for about 1 hour. By high speed mechanical dispersion, 2, 4 and 6 parts of nano-silica particles are

added to 100 parts of phenolic resin. Then the phenolic resin containing nano-silica is taken out and put into a mold with a doctor blade. After cooling to room temperature, the resin film has been prepared.

The preparation of composites is as follows. The prepared resin film is attached to the quartz fiber cloth. One lamination sequence (I) is: a film adhered to a layer of cloth. Another lamination sequence (II) is: a film adhered to two layers of cloth. After lamination, the nano-silica modified phenolic composites are prepared by RFI process. Finally, the single-layer and double-layer composite samples with different mass fractions of 0%, 2%, 4%, and 6% nano-silica particles are prepared.

2.3 Characterization

The rheological behaviors of nano-silica modified phenolic resins are studied by dynamic frequency sweep experiments to obtain their rheological spectra. Rheological runs are performed using an ARES Rheometer (TA Instruments) with a 25 mm upper plate and a 40 mm lower parallel plate; the gap was fixed at 1 mm. The operating condition during the rheological tests is: a frequency in 1 Hz, an applied strain of 2%, and a pre-shear of 10 s^{-1} applied to the samples for 30 s after a delay time of 10 min once the operating temperature is reached, in agreement with ASTM D 4440. In viscosity-temperature test, the operating temperature range from 50°C to 100°C, applying a heating rate of 1°C/min. The initial strain applied to the resins during the temperature sweep tests is 0.1%. The auto-strain option was enabled during the tests to keep the torque within the measurement range of the equipment. In viscosity-time

test, the operating temperature fix at 70°C, 80°C and 90°C with the test time of 50 min.

The curing behaviors of nano-silica modified phenolic resins are performed on a PerkinElmer LAB SYS-DSC 8500 calorimeter using medium pressure pans (ME-26929) at a heating rate of 10°C/min from 20 to 280°C under air atmosphere.

The microstructures of film surface and composite surface are studied by scanning electronic microscopy (SEM) in an ULTRA PLUS-43-13 microscope. Every sample is sputtered using Cr for 60 seconds in 10 mA under the pressure of 0.6×10^{-2} Pa, and is tested at 20 kV. The phenolic resin film with the nano-silica content of 4% is subjected to energy dispersive X-ray spectroscopy (EDS). Carbon and silicon elements are area scanned.

The mechanical properties of nano-silica modified phenolic composites are performed using a universal machine (INSTRON-1341) at room temperature. Three-point bending tests are performed according to the standard of GBT 1449, and a minimum of five specimens per test condition is tested. The basic principle of the test is that the specimen is loaded by universal material testing machine at constant loading rate through three-point bending without fixed support (without force), so that the specimen is destroyed or its deflection reaches 1.5 times of its thickness when it is crushed. The size of specimen for bending test is 80×15×4 mm. And the loading speed selected in the experiment is 1 mm/min. The bending strength, σ_f , is calculated based on the following formulae:

$$\sigma_f = \frac{3F_m l}{2bh^2} \quad (1)$$

Where F_m is the applied load (N) at the highest point of load-deflection curve, l is the span length (64mm), b is the width of the test specimens (15mm) and h is thickness of the test specimens (4mm).

3 Results and discussion

3.1 Rheological properties

As well known, the viscosity changes of polymer under different temperature conditions can be predicted by the double Arrhenius equation [28, 29]. Proper resin viscosity and sufficient low viscosity stable time determine the applicability of the RFI process. In order to the optimal design of the process system, the rheological properties of the nano-silica modified phenolic resins are first studied by the viscosity experiments.

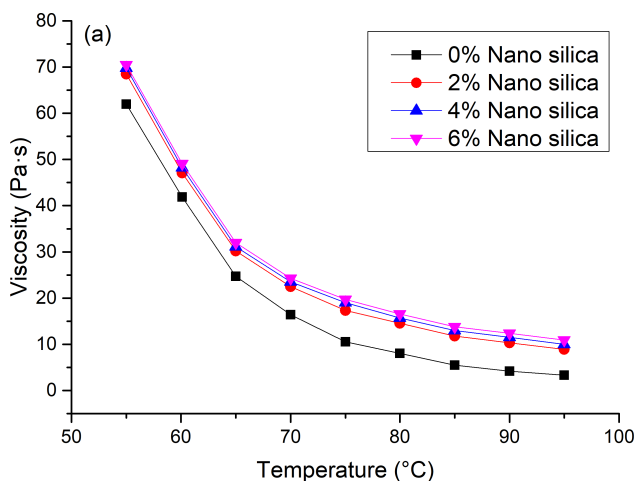


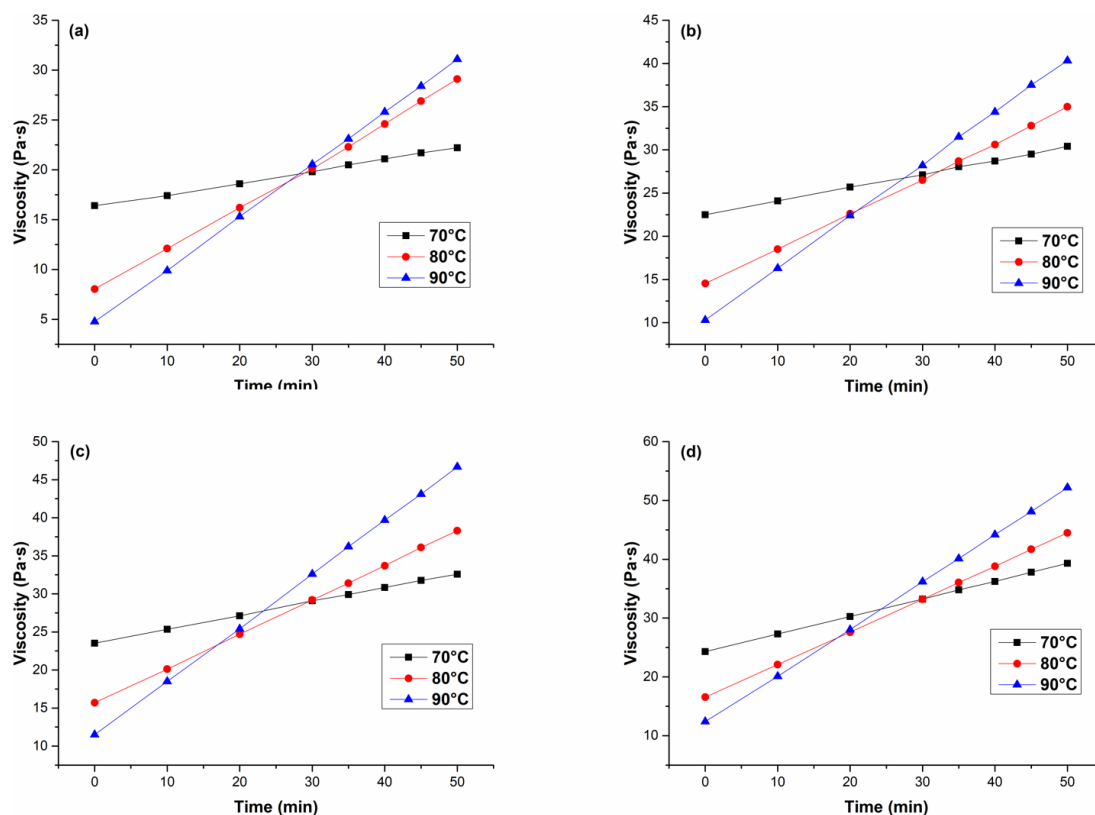
Figure 2: Viscosity-temperature curves for LCM phenolic resin

The viscosity-temperature characteristics of pure resin and nano-silica modified phenolic resins are tested in the range of 50°C to 100°C, and the test results are shown in Figure 2. As the temperature increases, the viscosity of nano-silica modified phenolic resins continues to decrease. Moreover, the viscosity of the resin increases after adding nano-silica particles, but with the addition of nano-silica particles, the effect is not so significant, in other words, the increase of resin viscosity is not large. It is obvious that the viscosity of resin is the lowest between 70°C and 90°C, and its viscosity can meet the requirements of RFI process. The viscosity is relatively stable at about 80°C. Therefore, the resin film infiltration temperature is considered to be 80°C.

The viscosity-time characteristics of pure resin and nano-silica modified phenolic resins are tested at 70°C, 80°C and 90°C, and the test results are shown in Table 1 and Figure 3. From the data in the table and figures, it is found that the viscosity of the resin increases with time at a constant temperature. In Figure 3, the tendencies of the viscosity change at 70°C, 80°C and 90°C are generally consistent when the nano-silica mass fraction is 0%, 2%, 4% and 6%. The viscosity at 90°C increases most rapidly with increase of time, while the viscosity at 70°C increases most gently. The speed of viscosity increase at 80°C is between the speed at 70°C and 90°C. And before 30 minutes, the viscosity at 80°C is between the viscosity at 70°C and 90°C. According to the resin film infiltration process, 80°C is selected as the resin film infiltration temperature, and the infiltration time is 30 minutes.

Table 1: Viscosity-time characteristics of neat phenolic resin

Temperature	Viscosity (Pa·s)							
	0min	10min	20min	30min	35min	40min	45min	50min
70°C	16.4	17.4	18.6	19.8	20.5	21.1	21.7	22.2
80°C	8.1	12.1	16.2	20.1	22.3	24.6	26.9	29.1
90°C	4.8	9.9	15.3	20.6	23.1	25.8	28.4	31.1

**Figure 3:** Viscosity-time curves for nano-silica content of (a) 0%, (b) 2%, (c) 4% and (d) 6%, respectively

3.2 Curing kinetics

As the RFI molding process is closed molding, if it is directly cured by a curing agent, it will generate small molecular substances, which results in poor surface finish of the product, so high temperature curing is adopted [30, 31]. The DSC test is used to analyze the curing reaction characteristics, and the data is shown in Figure 4.

The DSC of nano-silica modified phenolic resin exhibits two peaks: an endothermic peak and an exothermic peak. The endothermic peak generated at 100-130°C is caused by volatilization of the uncleaned solvent remaining in the resin, and may also occur with a partial polycondensation reaction of the phenol resin. Exothermic rate due to the reaction of the system is less than endothermic rate by the small molecules in the system, and as a result

it appears as an endothermic process. The para-position of the phenolic hydroxyl group reacts with formaldehyde to crosslink the system into a three-dimensional network structure at 170°C which is the large exothermic peak. The difficulty of curing phenolic resin depends on the apparent activation energy E of curing reaction. The smaller the activation energy is, the easier the curing reaction will be. It can be seen in Figure 4 that the addition of nano-silica particles does not have much influence on the curing of phenolic resin. And the curing temperature is concentrated at 150-170°C.

For different groups of sample, the cure peak of second group is the narrowest, that is, the time required for curing is the shortest. The resin needs to absorb a certain amount of energy to be cured. In general, a resin with a low apparent activation energy has a lower energy required for a cur-

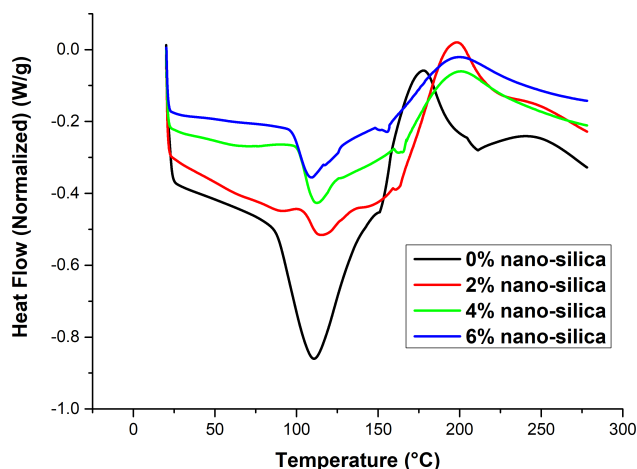


Figure 4: DSC curves of phenolic resin with nano-silica content of 0%, 2%, 4% and 6%

ing reaction, and a curing reaction is easier [35, 36]. When the nano-silica content is 2%, modified phenolic resin has the lowest apparent activation energy, indicating that it is easier to cure upon heating. In summary, the curing system of phenolic resin can be set to 130°C for 1h, followed by 150°C for 1h, and then 180°C for 1h. When the content of the nano-silica particles is 2%, the curing curve of the phenolic resin is steeper, and the curing peak is the narrowest, that is, the curing reaction is easier and faster, and is more suitable for the RFI molding process. However, the difference between the different groups of sample is so little that it almost does not affect the curing of phenolic resin. Therefore, the addition of nano-silica particles does not have significant influence on the curing of phenolic resin.

3.3 Infiltration

The scanning electron microscope images of nano-silica modified phenolic film is shown in Figure 5. As shown in Figure 5, nano-silica particles are embedded in phenolic resin matrix. The combination of particles and matrix is well, and no obvious interface is visible. When the content of nano-silica particles is more than 4%, agglomeration occurs. In order to verify the distribution of nano-silica particles on the surface of phenolic film, element surface scanning of 4% nano-silica modified phenolic film has been analyzed by EDS. Figure 6 shows the distributions of element C and Si on the film surface. Element C, as a characteristic element of resin, is evenly distributed in the form of matrix. Element Si, as a characteristic element of nanoparticle additives, is dispersed in the matrix. It is inferred that the nano-silica particles can be uniformly distributed with the maximum addition amount of 4%.

As we all know, nanoparticles can only be effective if they reach a certain amount of addition [37]. Therefore, it is necessary to further study the dispersibility of composites with the mass fractions of 4% and 6% nano-silica particles.

Figure 7 shows the microstructure of composites surface with 4% nano-silica particles. Figure 7a and Figure 7b are the resin surface and the fiber surface in sequence of a film adhered to a layer of cloth, respectively. Figure 7c and Figure 7d are the resin surface and the fiber surface in sequence of a film adhered to two layers of cloth, respectively. Regardless of the two lamination sequences, the nanoparticle content of resin surface is higher than that of fiber surface. It indicates that the fiber cloth hinders the penetration of nanoparticles during the RFI process. In comparison of two lamination sequences, there is a smaller difference between the front and back surface of sequence II than that of sequence I. It shows that sequence II is more reasonable, with fewer microstructural defects on the resin surface and the fiber surface.

Figure 8 shows the microstructure of composites surface with 6% nano-silica particles. Figures 8a and 8b are the resin surface and the fiber surface in sequence of a film adhered to a layer of cloth, respectively. Figure 8c and 8d are the resin surface and the fiber surface in sequence of a film adhered to two layers of cloth, respectively. When the nano-silica content is 6%, due to the agglomeration of nanoparticles, the content of nano-silica on the resin surface is much larger than that on the fiber surface. In Figure 8a and 8c, nano-silica particles on the resin surface are unevenly distributed. A large amount of resin and nano-silica particles remain in the resin surface. Some nano-silica particles are agglomerated together so that some fibers on the fiber surface are exposed. In Figure 8b and 8d, there is a clear interface between resin and fiber, and the microstructural defects are clearly visible.

Therefore, the infiltration property of the film containing 4% nano-silica is significantly better than that of the film containing 6% nano-silica. In the vacuum state, the infiltration distance of sequence II is more suitable for RFI forming process.

3.4 Mechanical properties

The composites with the lamination sequence II are used for the density, fiber mass fraction and mechanical properties test. Table 2 gives the average value and standard deviation of density, fiber mass fraction and bending strength.

It is known to all that the fiber mass fraction of composites has a direct influence on the mechanical proper-

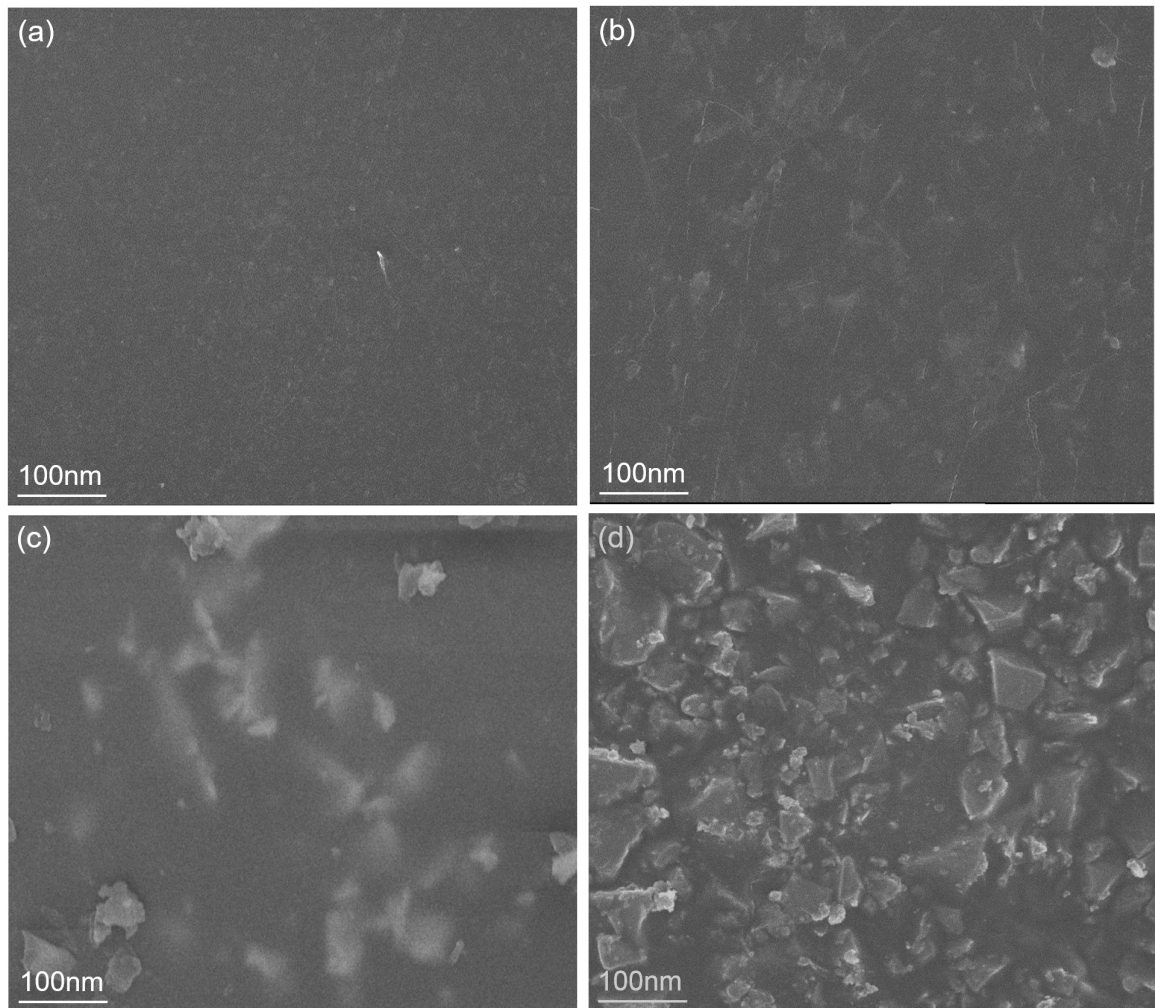


Figure 5: SEM images of nano-silica modified phenolic resin film of (a) 0%, (b) 2%, (c) 4% and (d) 6%

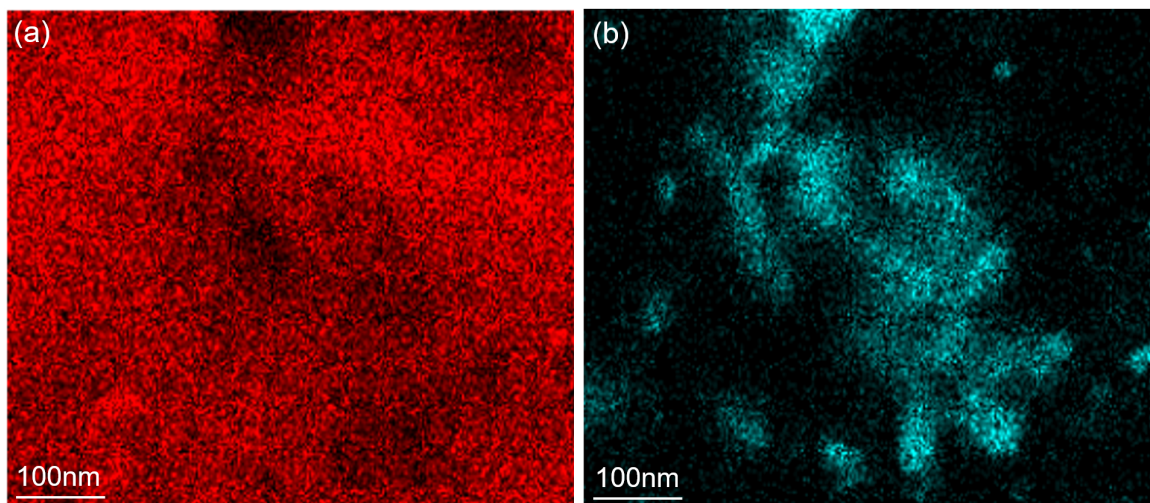
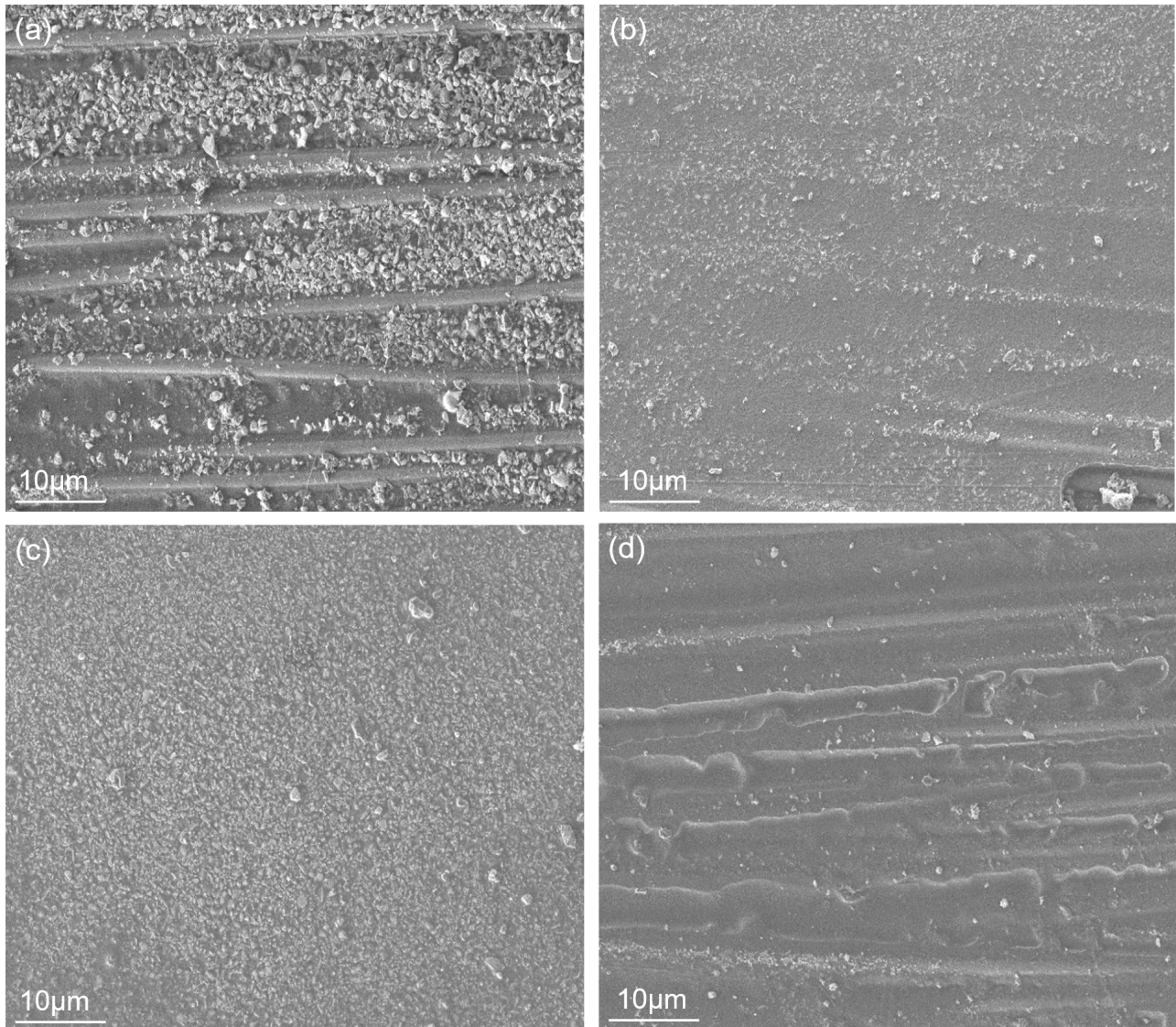


Figure 6: EDS images of modified phenolic resin film with 4% nano-silica (a) Element C and (b) Element Si

Table 2: Fiber mass fraction, density and bending strength of composites

Nano-silica mass fraction	Fiber mass fraction (wt.%)	Density (g/cm^3)	Bending strength (MPa)
0%	51.4 ± 0.9	1.58 ± 0.12	257.4 ± 9.5
2%	50.9 ± 1.1	1.62 ± 0.15	283.5 ± 10.8
4%	50.1 ± 0.9	1.64 ± 0.19	361.7 ± 11.4
6%	49.6 ± 1.2	1.65 ± 0.25	338.6 ± 12.6

**Figure 7:** SEM images of composites with 4% nano-silica: sequence I: (a) resin surface (b) fiber surface and resin film; sequence II: (c) resin surface, (d) fiber surface

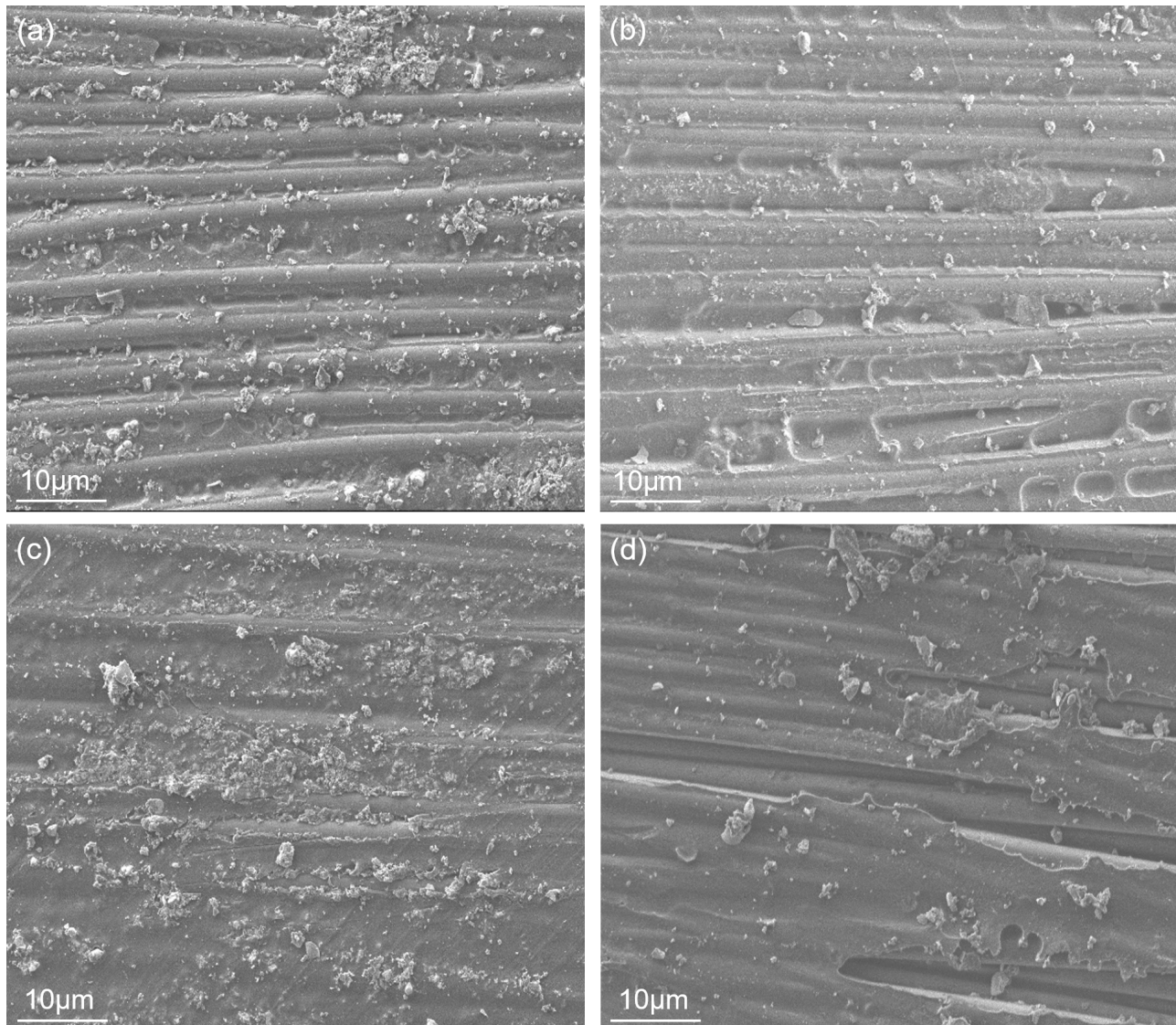


Figure 8: SEM images of composites with 6% nano-silica: sequence I: (a) resin surface, (b) fiber surface and resin film; sequence II: (c) resin surface, (d) fiber surface

ties of composites [38, 39]. The addition of nanoparticles definitely leads to the decrease of fiber content. From the results of Table 2, the fiber mass fraction decreases with the addition of nano-silica. In neat composites, the fiber mass fraction is 51.4%. And when 6% nano-silica is introduced, the fiber mass fraction is 49.6%. Under the condition of 6% maximum nano-silica addition, the difference of fiber mass fraction caused by particle addition is not significant. In other words, it is unlikely that the nanoparticles will cause changes in mechanical properties by causing changes in fiber mass fraction. However, the introduction of nanoparticles has indeed greatly improved the mechanical properties of composites. The bending strength of neat phenolic composites is 257.4 MPa, and the bending

strengths of modified phenolic composites with 2%, 4%, and 6% nano-silica particles are 283.5 MPa, 361.7 MPa and 338.6 MPa, respectively. It can be observed from Table 2, with the increase of the content of nano-silica particles, the bending strength of composites firstly increases and then decreases. The highest bending strength of composites occurs when the nano-silica content is 4%, and the highest value is 40.5% higher than the initial value of neat composites.

In the bending performance test, the upper surface of the material is subjected to stretching, while the lower surface of the material is subjected to compression, and there is also interlayer shearing inside the material [40]. Therefore, the improvement of bending properties can best rep-

resent the influence of nanoparticles on the mechanical properties of composites.

In this work, the size of nano-silica particle is less than 30 nm, which reflects its unique volume effect and surface effect. The enhancement mechanism of mechanical performance is mostly attributed to the special effect of nanoparticles. On the other hand, nanoparticles have the great ability of physical and chemical binding with matrix molecules. Uniformly distributed nanoparticles disperse in the matrix and strengthen the matrix, reducing defects while greatly increasing the strength of the composite. Thus, when the nano-silica content is 4%, the bending strength of composites is greatly improved by 40.5% than that of neat composites. However, with the further increase of nano-silica content, the flow performance of modified resin becomes worse, and some nano-silica aggregates together to form agglomerations. Defects occur during the RFI process. The uneven distribution of nanoparticles and the generation of defects can cause the mechanical properties to drop again.

4 Conclusions

Different mass fractions of nano-silica particles are introduced into phenolic resin to prepare composite materials by RFI process which improves its mechanical properties. The infiltration of film and the properties of composites are characterized by the rheological test, DSC, SEM, EDS, and mechanical test. The major conclusions are presented below.

1. The proper temperature and time of resin film infiltration are 80°C and 30 minutes, respectively. After the RFI process, the curing process curve is at 130°C for 1 h, at 150°C for 1 h and at 180°C for 1 h. The curing process system is a stepwise curing process. The addition of 2-6% nano-silica has no significant effect on the curing of the composite.
2. On both lamination sequences, in comparison with the resin surface and the fiber surface, the optimal addition amount of nano-silica is 4%. When the mass fraction of the nano-silica is 4%, the distribution of nanoparticles on the resin surface is the most uniform, and the nanoparticles infiltrated on the fiber surface have the highest content and the most uniform distribution. The infiltration property of modified phenolic film containing 4% nano-silica is significantly better than those of nano-silica modified phenolic films containing other mass fractions.
3. With the increase of nano-silica content, the mechanical properties of composites increases continuously. And when the mass fraction of nano-silica is 4%, the composites have the maximum value of bending strength. The bending strength of nano-silica modified phenolic composites increases by 40.5%, compared to that of neat phenolic composites.

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