Preparation, characterization and properties of amine-functionalized silicon carbide/polyimide composite films

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High performance amino-functionalized silicon carbide/polyimide (m-SiC/PI) composite films were prepared using a straightforward polycondensation, and the nanoparticles (NP) obtained were modified using 3-aminopropyl-trimethoxysilane. The presence of amine functional groups made dispersions of m-SiC NP in dimethylacetamide more homogeneous and uniform. Their structures and stabilities were investigated using X-ray diffraction, scanning electron microscopy and zeta-potential analysis. The thermal stability and the tensile strength of the m-SiC/PI composite films improved with increasing m-SiC NP content, for example the inclusion of 3 wt% m-SiC NP increased the tensile strength and Young’s modulus by 41.1% and 40.1%, respectively. The morphology of the cross-section revealed that breakage within these composite films was the result of ductile fracture, whereas for pure PI film it was caused by brittle fracture.

1. Introduction

Nanoparticles (NP) of reinforced polyimide (PI) composites have attracted increasing interest for a number of applications because of their high strength, thermal stability and multifunctionality. Silicon carbide (SiC) NP-reinforced PI composites are characterized by outstandingly low thermal expansion, low permittivity (low-k) and high thermal conductivity, and are extensively employed in electronic packaging, electrical insulation and in radiators. However, these nanocomposites are difficult to produce because of a number of serious technical challenges, for example they need to be cured at high temperatures and must be soluble in high boiling point solvents such as dimethylacetamide (DMAC) or N-methylpyrrolidone (NMP). Another critical challenge has been the agglomeration and non-uniform distribution of NP in the PI matrix during the preparation process.

Over the past decade much effort has been expended to improve the dispersion of NP and to modify the interface between NP and the PI matrix, in particular by grafting on active functional groups or by employing solid-state polymerization. The choice of a coupling agent, for example an amphiphilic molecule, can be valuable for enhancing the dispersibility and compatibility of SiC NP within the PI matrix. For example, a hydrophilic functional group might be able to react with the SiC surface, and other hydrophobic functional groupings might react with groups in the PI matrix. The functional groups (e.g., Si–OH or NH2) provide an enhanced interface between the different materials involved. Over the years, more efficient silane coupling agents have been developed, including amine-functional silanes, glycidyl silanes, chlorinated silanes and silsesquioxanes. However, the surfaces of SiC NP tend to be very smooth and inactive, making the modification and improvement of surface activity by grafting difficult. In particular, when the SiC content is above 2 wt%, agglomerates of SiC NP limit the improvement in mechanical properties of the SiC/PI composites.

In the present study, activated SiC-SiO2 NP were prepared by first annealing at 700 °C for 2 h. This process overcame the presence of inactivated surfaces, which limited the original SiC NP by thermal oxidation of the SiC NP surface. Following this, amino (–NH2) functional groups were grafted onto the SiC–SiO2 NP using 3-aminopropyl-trimethoxysilane (APTMS) as a coupling agent, thus improving their compatibility and dispersibility within the PI matrix. The chemical structures and dispersion properties of SiC–SiO2 and SiC–SiO2–NH2 NP were investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and zeta-potential analysis. The thermal stability of the SiC/PI composite films was established by thermal analysis. The mode of fracture was also investigated in cross-section by SEM to detect evidence of ductile rupture.
2. Experimental

2.1 Thermal oxidation of SiC NP

Fig. 1(a) is a schematic diagram of the thermal oxidation of SiC NP. The SiC NP were used as obtained (Hefei Kaier Nanometer Energy & Technology Co. Ltd, China) and were washed three times in succession using deionized water and absolute ethanol in turn. The resulting SiC NP were placed in a porcelain boat and heated at 10 °C min⁻¹ in a thermal treatment oven (MTI Corporation, OTF-1200X) in an oxygen atmosphere and then held at either 500 °C or 700 °C for 1 h, the resulting SiC–SiO₂ NP being denoted as SiC-500 or SiC-700, respectively. After cooling, the SiC–SiO₂ NP were collected and further modified using the coupling agent, APTMS (Sinopharm Chemical Reagent Beijing Co. Ltd, China). Finally, the SiC–SiO₂ NP were dried in a vacuum oven at 80 °C for 4 h in a water bath. The reaction products were centrifuged and washed several times with anhydrous ethanol. Finally, the SiC–SiO₂ NP were collected and further modified using the coupling agent, APTMS (Sinopharm Chemical Reagent Beijing Co. Ltd, China).

2.2 Amine functionalization of the SiC–SiO₂ NP

Fig. 1(a) also outlines the amine-functionalization of SiC–SiO₂ NP, a key step in the preparation of the high performance m-SiC/PI composite films.

SiC@SiO₂ NP (0.1 g) were placed in a three-necked flask containing 100 mL of absolute ethanol. After mixing ultrasonically for 30 min, 0.3 mL of APTMS was added dropwise to the homogeneous SiC–SiO₂ dispersion and then held at 78 °C for 4 h in a water bath. The reaction products were centrifuged and washed several times with anhydrous ethanol. Finally, the m-SiC NP were dried in a vacuum oven at 80 °C for 6 h. The coupling agent, APTMS, was then used to modify the SiC–SiO₂ NP.

2.3 Preparation of the SiC/PI composite films

Fig. 1(b) and (c) illustrate the synthesis of polyamide acid (PAA) and the preparation of m-SiC/PI composite films. PAA was prepared by polycondensation of benzophenone-tetracarboxylic dianhydride (BTDA) and 4,4’-diaminodiphenyl ether (ODA) at a molar ratio of 1 : 1.02 in DMAC. In order to prepare the m-SiC/PI composite films, different proportions of m-SiC NP, i.e., 0.5 wt%, 1 wt%, 2 wt% or 3 wt%, were added to the PAA solution. After stirring ultrasonically for 2 h, an homogeneous solution of m-SiC and PAA was obtained and this could be cast on a clean glass substrate and cured progressively at 70 °C/5 h → 100 °C/2 h → 200 °C/1 h → 300 °C/1 h in a vacuum oven. Finally, m-SiC/PI composite films were obtained after immersion in boiling water for 30 min.

2.4 Characterization

The morphology of the m-SiC NP and the m-SiC/PI composite films was determined by optical microscopy (Shanghai Longway Optical & Shanghai Yueping Scientific Instruments Co., Ltd. LW-300), SEM (FEI Quanta 2000) and transmission electron microscopy (TEM; Hitachi 5570). The structures of the m-SiC NP and the m-SiC/PI composite films were recorded with an XRD (Rigaku D/Max-RB) using Cu Kα (λ = 1.54178 Å) radiation. FTIR spectroscopy (Nicolet AVATAR 360) was used to characterize the composition and chemical structure of the original SiC and m-SiC NP. Zeta-potential analysis (Malvern Instruments ZEN 3690) was used to study the dispersion stability of the SiC and m-SiC NP in DMAC. Thermal stability was assessed by thermogravimetric analysis (TGA) and differential thermal analysis (TA Instruments Q2000). Mechanical properties were measured on an INSTRON 5569 electromechanical testing system at room temperature. Additionally, the cross-sectional morphology of m-SiC/PI composite films were examined by SEM.

3. Results and discussion

Fig. 2 shows XRD patterns of the SiC NP before and after annealing at 500 °C and 700 °C. The results for the original SiC NP were in good agreement with the Joint Committee on Powder Diffraction Standards data (JCPDS card 74-2307) for the β-SiC phase. The SiC NP annealed at 500 °C did not produce the obvious SiO₂ shell on the surfaces of SiC NP. The relative
intensity and peak position of SiC-700 (SiC–SiO2) NP were almost coincident with the standard β-SiC and SiC-500 NP, apart from a broad peak of SiO2 between 2θ 18° to 30°. This confirmed that the annealing process had been an effective method for improving the reactivity of the SiO2 shell of the SiC NP, while maintaining the integral structure of the core.

Fig. 3 shows FTIR spectra of the different SiC samples. An obvious absorption peak between 800 and 900 cm⁻¹ was present in every SiC sample (Fig. 3(a)–(d)) before and after annealing and modification, and was assigned to the stretching vibration peak of Si–C bonds.²⁸ Compared with the original SiC and SiC-500 NP, a strong absorption peak at 1067 cm⁻¹ appeared after annealing at 700 °C (Fig. 3(c) and (d)), assigned to the stretching vibration peak of Si–O bonds.²¹ This indicated that the oxidation reaction at 700 °C had successfully formed a SiO2 shell on the SiC core. In addition, the SiC–SiO2–NH2 NP presented a broad peak centred around 3386 cm⁻¹, which corresponded to the stretching vibration peak of the N–H bonds of the amine functional groups and confirmed that amine functionalization had been achieved. Furthermore, the stretching vibration peak at 2885 cm⁻¹, assigned to –CH₃– bonds from the APTMS,²² and a vibration peak at about 1610 cm⁻¹, assigned to N–H bonds,²³ were observed in the SiC–SiO2–NH2 NP, further confirming these conclusions.

Fig. 4 shows SEM micrographs of SiC and m-SiC NP before and after annealing at different temperatures (500 and 700 °C). As seen in Fig. 4(a)–(c), these unmodified SiC or SiC–SiO2 NP were agglomerated and crosslinked with each other, because of the mutual interactions.²⁴ Furthermore, a reorganization phenomenon was also quite significant in the original SiC and SiC-500 NP (Fig. 4(b)). Furthermore, the size of the m-SiC NP (Fig. 4(d)) was certainly increased and the shapes became more regular, homogeneous and better dispersed, because of the absence of grain-stacking or agglomeration.²⁵ These results demonstrated that the m-SiC NP were stable and not readily reunited.

In principle, the surface states of the SiC NP supplied their surface charges, probably because of the dissociative or selective absorption of the charged ions.²⁶ To maintain their electric neutrality, these charged surfaces would attract counterions of equal charge on the outside, described as an electric double-layer (EDL).²⁷ An EDL provided homogeneous dispersions of the SiC or m-SiC NP in DMAC and PAA solution.

The zeta-potential indicates the potential between two layers of mutual movement in the EDL and one point in the solution, when the dispersed NP were subject to the action of an external electric field. The zeta-potential analysis can, therefore, be used to evaluate the stability of colloidal solutions,²⁸ by measurement of the attractive and repulsive forces of the SiC NP. A larger zeta value means that the attractive force is greater than the repulsive force between NP, and the solution is thus more stable. Conversely, a smaller zeta-potential implies that the solution is less stable and more likely to settle out.²⁹

Fig. 5 shows the curves illustrating the relationship between the zeta-potential and the pH value in ethanol. The isoelectric point of the original SiC NP was at pH 7.2, meaning that the
hydroxyl (–OH) radicals on the SiC surface reacted with hydrogen ions (H+) at pH < 7.2 to form –OH₂⁺. The positive zeta-potential value of SiC NP at pH 7.2 or above was because of the positive charge on the surface. The isoelectric points of SiC-500 and SiC-700 (SiC–SiO₂) NP occurred at pH 3.9 or 4.0, respectively. Since the PAA solution was acidic, the annealed SiC NP were probably modified and transferred their surface electric properties, improving the dispersion stability of the PAA.

On the other hand, the isoelectric point of the m-SiC NP was at pH 8.45. The zeta-potentials of m-SiC NP were higher than those of the original SiC NP under acidic conditions. This indicated that among these SiC NP, the m-SiC NP had the best stability in PAA. Furthermore, the –NH₂ and –OCH₃ groups of the m-SiC NP surfaces from APTMS also enhanced the compatibility between m-SiC NP and the PI matrix. The SiC–SiO₂–NH₂ NP were thus able to enhance the dispersibility and mechanical properties of the SiC/PI composite films.

Fig. 6 shows the XRD patterns of the m-SiC/PI composite films. The characteristic peak at 2θ = 18.6°, representing amorphous PI, is clearly observed. Other diffraction peaks of SiC NP are also observed at 2θ = 35.64°, 59.96° and 71.76°, assigned to standard JCPDS card 74-2307. This result confirmed the presence of SiC NP in the SiC/PI films. However, the diffraction peak width around 2θ = 18.7° broadened with increasing SiC content, because of the increasing interaction between SiC NP and PI molecules. The presence of SiC NP thus promoted the structural reorganization of PI films.

Fig. 7(a–j) show optical micrographs of SiC/PI and m-SiC/PI composite films. The dispersions of m-SiC NP in the PI matrix were homogeneous. Even when the m-SiC contents were as high as 3 wt% no obvious agglomeration was observed. The surface morphologies of m-SiC/PI composite films are shown in Fig. 7(k–o). Although different levels of structural defects appeared on the surface of m-SiC/PI composite films, there was no obvious agglomeration of the m-SiC NP in the PI matrix. This confirmed the good dispersibility of m-SiC NP in the PI matrix.

To further study the influence of m-SiC NP dispersion on thermal stability, thermal analysis (TGA) was employed to investigate the m-SiC/PI composite films. Fig. 8 shows the TGA curves of m-SiC/PI composite films under nitrogen heated at a rate of 10 °C min⁻¹. Compared with the pure PI film, the heat resistance of m-SiC/PI composite films clearly improved with increasing SiC NP content.

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**Fig. 6** XRD patterns of the m-SiC/PI composite films for different SiC contents.

**Fig. 7** Optical micrographs (a–j) and SEM micrographs (k–o) of SiC/PI and m-SiC/PI composite films with various SiC contents: (a), (f) and (k), pure PI films; (b), (g) and (l), SiC/PI, 0.5 wt%; (c), (h) and (m), SiC/PI, 1 wt%; (d), (i) and (n), SiC/PI, 2 wt%; (e), (j) and (o), SiC/PI, 3 wt%.
The insert in Fig. 8 shows the temperatures at which a weight loss of 5% ($T_{d5}$) and 10% ($T_{d10}$) of the m-SiC/Pi composite films was observed. The comparative analysis shows that the m-SiC/Pi composite films with 3 wt% m-SiC NP content had the highest $T_{d5}$ and $T_{d10}$, at 558.3 °C and 579.8 °C, respectively. The results also confirm that the m-SiC NP were well dispersed in the PI matrix, and demonstrate the resulting improvement in heat resistance. In addition, the bonding effect of m-SiC NP to the PI matrix was strengthened because of the improved chemical compatibility.\textsuperscript{37}

In order to detect the distribution of SiC NP in the PI matrix, the SiC/PI composite film was cut into a thin plate and transferred to a copper grid. The TEM technique was employed to characterize the SiC NP distribution.

Fig. 9 shows TEM micrographs of SiC/PI and m-SiC/PI composite films. At an SiC content of 1 wt% in the PI matrix (Fig. 9(a), (b), (e) and (f)), the micrographs confirm that the m-SiC NP were homogeneously distributed in the PI matrix. Furthermore, the unmodified SiC NP were clearly agglomerated. Because the surface energy of the SiC NP was reduced and the stability was improved, this provided a way of improving the mechanical properties of m-SiC/PI films.\textsuperscript{34} Although the m-SiC NP content in the PI matrix was increased to 3 wt% (Fig. 9(g) and (h)), the distribution of SiC NP in the PI matrix remained uniform, and was much better than for the unmodified SiC NP (Fig. 9(c) and (d)). Because of the improved dispersion and compatibility of the m-SiC NP in the PI matrix, the m-SiC/PI composite films provided a better interaction between the m-SiC NP and the PI molecules.\textsuperscript{35} The results of optical microscopy and the SEM micrographs support this conclusion.

For a better understanding of the enhancement of SiC and m-SiC NP, the tensile performance was investigated. Fig. 10(a) and (b) show typical stress–strain curves of SiC/PI and m-SiC/PI composite films, from which it is clear that the values of tensile strength and Young’s modulus, calculated at the linear elastic deformation stage, increased with increasing SiC content.\textsuperscript{38}

Fig. 10(c) illustrates the relationship between tensile strength and SiC content. It is seen that the tensile strength of m-SiC/PI composite films were much higher than those of SiC/PI composite films, a result of the good compatibility of the m-SiC NP and the PI matrix and the interaction between them.\textsuperscript{39} When the SiC content exceeded 2.5 wt% the tensile strength of the SiC/PI composite films decreased. This is because of the large agglomerates restraining the enhancement effect of SiC NP on the PI films. When the m-SiC content was 3 wt%, the tensile strength of m-SiC/PI composite films increased to 41.1% than that of the pure PI film and by 15.3% more than that of the unmodified SiC/PI composite film.

Fig. 10(d) shows the relationship between Young’s modulus and SiC content. When the SiC content reached 2.5 wt%, the Young’s modulus reached a maximum before modification, and when SiC content was 3 wt%, the Young’s modulus was quickly reduced. Furthermore, for m-SiC NP the Young’s modulus was significantly increased.\textsuperscript{40,41} In particular it was found that even when the SiC content was as high as 3 wt%, the Young’s modulus of the m-SiC/PI composite films was not reduced – on the contrary, it was 40.1% greater than that of the pure PI film.

The SEM technique was also used to study cross-sections under tensile fracture. Fig. 11 shows SEM micrographs of the
SiC/PI and m-SiC/PI composite films with 3 wt% SiC content. In Fig. 11(a) and (b) it is seen that the cross-section of the SiC/PI composite film contained reunited grains of SiC NP at the surface of the fracture. The reunited grains would tend to increase the stress concentration and render the surface of the fracture crack smooth. However, the m-SiC/PI composite films with 3 wt% SiC content presented an increased toughness fracture, as seen in Fig. 11(c) and (d), indicating that the tensile strength and modulus of elasticity had clearly increased compared with those of the unmodified SiC/PI composite film.

There were two main reasons for these conclusions. Firstly, the crosslinked nature of the m-SiC NP and the PI matrix was more effective for the transmission of stress, and thus, stronger external forces were required for tensile failure. Secondly, the amino-functional groups on the surface of m-SiC NP improved the compatibility and dispersibility of the m-SiC NP and the PI matrix. The good dispersion of m-SiC NP in the PI matrix allowed the stress concentration to be overcome.

4. Conclusions

We have developed a simple but highly efficient method for the preparation of high-performance m-SiC/PI composite films. The SiC NP were annealed at 700 °C for 1 h before modification with APTMS. m-SiC/PI composite films with a range of SiC contents were successfully produced using a solution blending technique. The FTIR spectra and zeta-potential of the m-SiC NP demonstrated that the amine functional groups had been effectively grafted onto the SiC NP. This functionalization improved the dispersion of 3 wt% m-SiC NP in the m-SiC/PI composite films without reaggregation, which was confirmed by SEM and TEM micrographs. After modification with APTMS, TGA measurements demonstrated that the thermal resistance and stability of the m-SiC/PI composite films had been significantly improved: the tensile strength was increased by 30% and the modulus of elasticity increased by 13.67%. SEM micrographs showed that there were no obvious reunion grains or crack distribution in the fracture surface. The anti-cracking ability of the films was significantly improved by the uniform dispersion of m-SiC NP in the PI matrix. This study is expected to be of benefit in a number of potential applications, for example functional coatings, anti-corrosive and dielectric materials, and gas sensors.
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