Structural and thermal characterization of polyvinylalcohol grafted SiC nanocrystals

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1. Introduction

Recent years have seen a tremendous progress in the realm of wide bandgap materials, as devices fabricated using such materials promise a substantial improvement in their performance. Moreover, their ability to operate at higher temperatures, power densities, higher voltages and higher frequencies make them highly suitable for use in future electronic systems. Thus, silicon carbide (SiC) a well renowned covalent ceramic material is a potential candidate for such applications because of its superior mechanical properties (strength, stiffness and hardness) [1], chemical (oxidation and corrosion resistance) [2] and thermal stability at high temperatures [3]. Owing to the extraordinary properties exhibited by SiC nanocrystals, they are being studied extensively as nanofillers for the synthesis of polymer based nanocomposites with improved electrical, thermal, and mechanical properties [4–6]. However, because of the presence of strong vander waals interactions among the SiC nanocrystals and low compatibility of SiC nanocrystals with most of the polymers, the dispersion of SiC nanocrystals in a polymer matrix is a big challenge [7, 8].

In order to expand the domain of applications and to harness the full potential of SiC nanocrystals, they must be well dispersed and should exhibit good interfacial interaction with the host matrix. Novel methods are being tried to improve the interfacial interaction and compatibility of SiC nanocrystals in polymer matrices [9–12]. Zhou et al have prepared SiC/diglycidyl ether of bisphenol-A glycidol ether epoxy resin/2-ethyl-4-methylimidazole (nano-SiC/DGEBA/EMI-2,4) composites by surface treatment of SiC nanoparticles to avoid agglomeration of nanoparticles [13]. Peled et al have performed surface modification of SiC nanoparticles with triethoxy-2-thienylsilane organosilane to obtain SiC-grafted-thiophene nanoparticles which contains groups that act as nucleation points for the polymerization of 3-thiopheneacetic acid (TAA) monomer [14]. Attachment of functional groups on the surface of SiC nanostructures is expected to significantly enhance dispersion and hence properties and applications of SiC nanocrystals embedded nanocomposites. The functionalization in a small area around the SiC nanostructures has been shown by Fradetal et al in order to enhance the performance of sensors [15]. Our group has also shown considerable enhancement in conductivity and microhardness of PVA after incor-
poration of functionalized SiC nanocrystals in PVA matrix [16]. Incorporation of inorganic nanoparticles such as SiC nanocrystals in host matrices for device fabrication requires a detailed understanding of surface reactivities of nanocrystals and of the filler-host compatibility and properties. With this aim, we report a novel route to the best of our knowledge for the surface modification and introduction of functional groups onto the surface of SiC nanocrystals for its enhanced reactivity and better dispersion properties.

In this work after surface modification, polyvinyl alcohol (PVA) was grafted onto the surface of SiC nanocrystals (PVA-g-SiC nanocrystals). PVA being a hydrophilic and biodegradable polymer has large technological and pharmaceutical applications [17, 18]. PVA was chosen as a host matrix because it has the desired solution properties in water and contains many isolated hydroxyl functional groups, which can adsorb organic molecules and transition metal ions with a high adsorption capacity based mainly on hydrogen bond interactions. No reports are available in literature on grafting of PVA on SiC nanocrystals. Therefore, in the present work, a technique to graft PVA onto the surface of SiC nanocrystals (PVA-g-SiC nanocrystals) has been presented. For grafting a layer of polymer on the surface of SiC nanocrystals a mixture of nitric acid and sulphuric acid has been utilized. There are hardly any reports available for the role of acidic solution for functionalization of SiC nanocrystals but grafting by using an oxidative process with a mixture of acids has helped to improve their interfacial interactions with polymers. Structural and thermal characterization of as received SiC and PVA-g-SiC nanocrystals was done in order to validate the presence of PVA on the surface of SiC nanocrystals.

2. Experimental

2.1. Materials

Analytical reagent grade PVA (molecular weight = 125 000 g mol\(^{-1}\)) obtained from Ranbaxy was used as received. The reaction utilized for the formation of SiC nanocrystals was the solid phase reaction of carbon with molten silicon which resulted in particle size in the range of 50–150 nm. The silicon powder with crystal sizes in the range 200 nm–5 µm was uniformly mixed with carbon black (Vulcan\(^{®}\) XC-72) in a 1:1 molar ratio with the help of a pestle and mortar. The mixture was transferred into an alumina crucible and heated to a temperature of 1525 °C ± 25 °C in a tubular furnace for 6 hr in an argon flow of 250–300 ml min\(^{-1}\). The furnace was heated and cooled at the rate of 5 °C min\(^{-1}\) [19].

2.2. PVA grafting

500 mg of SiC nanocrystals were suspended in 100 ml mixture of concentrated sulfuric acid and concentrated nitric acid (1:1) for 6 hr with ultrasonicator. The SiC nanocrystals were separated by centrifugation and washed with deionized water 3–4 times and dried at 50 °C in oven for 4 hr. For grafting procedure, 1 g PVA was mixed with 80 ml ethylene glycol in a beaker and heated to 140 °C while stirring vigorously on a magnetic stirrer. A transparent and viscous solution was obtained after stirring the solution for 4 hr. Temperature was then adjusted to 90 °C and oxidized SiC nanocrystals were added to the PVA solution. The resulting solution was homogenized upon stirring followed by ultrasonication for 3–4 h resulting in a black dispersion. The precipitates were allowed to settle down, washed several times with deionized water. Finally the PVA-g-SiC nanocrystals were dried in the oven at 50 °C.

2.3. Characterization techniques

ABB (MB 3000) fourier transform infrared spectrometer and a Dilor Raman spectrometer with resolution of 3–5 nm at 532 nm wavelength laser were used to ascertain the presence of fundamental vibrations of PVA in PVA-g-SiC nanocrystals in the range of 4000–400 cm\(^{-1}\). X-ray diffraction measurements were made using Bruker AXS D8 Advance diffractometer using CuK\(_\alpha\) radiation having 0.154 nm wavelength in the angle region from 20° to 80°. For transmission electron microscopic investigations, a small drop of the suspension of PVA-g-SiC nanocrystals was put on a carbon-coated copper grid. After drying the grid morphological studies were carried out by employing a Hitachi-H7500 transmission electron microscope operated at 80 kV. Surface morphologies of SiC nanocrystals were examined using a JEOL model JSM—6390LV scanning electron microscope.

After structural characterization, these nanocrystals were thermally characterized using Perkin Elmer Diamond STA 6000 TG/DTA analyzer at a heating rate of 10 °C min\(^{-1}\), from room temperature up to 700 °C, in air atmosphere at a flow of 20 ml min\(^{-1}\). TGA results were used to obtain the grafting degree (\(g_g\)), by the weight difference of SiC nanocrystals before and after the grafting reaction. The grafting degree has been determined by the following equation [20],

\[
g_g = \frac{W_g - W_o}{W_o} \times 100
\]

where \(W_g\) and \(W_o\) are the weights of the PVA-g-SiC and as received SiC nanocrystals, respectively.
3. Results and discussion

FTIR spectroscopy has been used to study the modifications introduced in the SiC nanocrystals before and after the grafting procedure. Figure 1 shows the FTIR spectra of as received SiC nanocrystals and PVA-g-SiC nanocrystals and inset shows the enlarged view of fingerprint region.

In the FTIR spectra of as received SiC nanocrystals (figure 1, curve (a)), a sharp peak at 785 cm\(^{-1}\) with a shoulder at 910 cm\(^{-1}\) has been observed which is ascribed to the Si–C stretching vibration of nanocrystals [21]. However, in the spectrum of PVA-g-SiC nanocrystals (figure 1, curve (b)), the intensity of characteristic Si–C vibration at 785 cm\(^{-1}\) is enhanced significantly as compared to as received SiC nanocrystals. Besides the amplified intensity of Si–C vibrational peak, certain additional peaks are also observed in the spectra of PVA-g-SiC nanocrystals. Distinct peaks observed at 1750 cm\(^{-1}\) and 1140 cm\(^{-1}\) corresponds to the C=O stretching vibrations of carbonyl group and C–O stretching vibrations. Wide band between 3000–3600 cm\(^{-1}\) is attributed to O–H stretching vibrations, and the peaks appearing at 2940 and 2845 cm\(^{-1}\) represent \(–\text{CH}_2–\) asymmetric and symmetric stretching vibrations, respectively [22]. Hence, the increase in the intensity of characteristic Si–C peak and the formation of new peaks in the PVA-g-SiC nanocrystals indicated that the surface of SiC nanocrystals have been modified after grafting with PVA.

The presence of PVA on the surface of SiC nanocrystals was further confirmed using Raman spectroscopy. Figure 2 shows the Raman spectra of as received SiC and PVA-g-SiC nanocrystals. In the Raman spectra of as received SiC nanocrystals, peaks at 786 cm\(^{-1}\) and 954 cm\(^{-1}\) corresponds to the transverse optical (TO) and longitudinal optical (LO) modes of the SiC nanocrystals [23, 24] however, after grafting PVA onto the surface of SiC nanocrystals, these modes are shifted to lower wavenumber i.e. 766 cm\(^{-1}\) and 913 cm\(^{-1}\) respectively. The full width at half maximum of these observed peaks lie in the ranges of 30–50 cm\(^{-1}\) for the TO mode and 40–50 cm\(^{-1}\) for the LO mode, which are quite large as compared to the values obtained for as received SiC nanocrystals.

The low intensity bands appearing at 1356 cm\(^{-1}\) and 1582 cm\(^{-1}\) in the spectra of as received SiC nanocrystals corresponds to the disorder D band and graphitic G band respectively. In case of PVA-g-SiC nanocrystals these D and G bands became more pronounced and shown a shifting of ~25 cm\(^{-1}\) towards lower wavenumber i.e. 1331 cm\(^{-1}\) and 1557 cm\(^{-1}\) respectively. Modifications observed in the D and G bands may be attributed to the changes introduced onto the surface of SiC nanocrystals as a result of PVA grafting. The ratio between the intensity of the D band and the intensity of the G band, denoted as \(I_D/I_G\), is considered as an indicator of the degree of disorder in the PVA-g-SiC nanocrystals and is presented in table 1. From the table 1 it can be clearly discerned that \(I_D/I_G\) ratio increases after grafting. An increase in this ratio for PVA-g-SiC nanocrystals corresponds to a high proportion of sp\(^3\) carbon, which is generally attributed to the presence of structural defects and provides the proof for the grafting process [25]. Hence, the changes observed in Raman as well as in FTIR spectra of as received SiC nanocrystals show that the SiC nanocrystals have been successfully grafted with PVA.

In order to substantiate that the grafting process has altered only the surface of SiC nanocrystals, XRD studies were carried out on as received SiC nanocrystals and PVA-g-SiC nanocrystals and the results are shown in figure 3. Figure 3(a) shows the XRD spectra of as received SiC nanocrystals. Peaks corresponding to SiC planes are observed at 2\(\theta\) values of 35.4\(^o\), 40.9\(^o\), 59.5\(^o\), 71.4\(^o\) and 75.1\(^o\) and are due to diffraction from (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes respectively. These peaks are consistent with the peaks of SiC available in JCPDS file no.
In the XRD spectra of PVA-g-SiC nanocrystals (figure 3(b)), peaks are observed at the same 2θ values however the intensities of the SiC peaks are reduced considerably after grafting PVA onto the surface of SiC nanocrystals which may be due to the coverage of SiC planes with PVA. Occurrence of peaks at the same 2θ values clearly shows that the crystalline structure of SiC nanocrystals remains intact even after grafting with PVA. Moreover, a low-intensity peak can be seen at 26.38° in the XRD spectra of PVA-g-SiC nanocrystals which can be attributed to the (0 0 2) reflection of carbon (JCPDS file no. 41-1487) [29]. As can also be seen from the Raman spectra of PVA-g-SiC nanocrystals that the appearance of D and G bands which are due to the carbon related structures has been intensified. Hence, the presence of polymer layer on SiC nanocrystals has altered the free carbon content in the nanocrystals.

XRD pattern was further used to calculate the average size of SiC nanocrystals from the full width at half-maximum (FWHM) of the major peak, using the Debye- Scherer equation [30],

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$  

(2)

Table 1. $I_D/I_G$ ratio of as received and PVA-g-SiC nanocrystals.

<table>
<thead>
<tr>
<th>SiC nanocrystals</th>
<th>D peak</th>
<th>G peak</th>
<th>$I_D/I_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received</td>
<td>1356</td>
<td>1582</td>
<td>0.9</td>
</tr>
<tr>
<td>PVA-g-SiC</td>
<td>1331</td>
<td>1557</td>
<td>1.1</td>
</tr>
</tbody>
</table>
where $\lambda$ (= 0.154 nm) is the wavelength of the CuK$_\alpha$ radiation source, $\beta$ is the full width at half maximum in radians, and $\theta$ is the angle between the incident ray and the scattering planes. Interplanar distance ($d$) between the crystal planes was determined using the formula,

$$d = \frac{n \lambda}{2 \sin \theta}$$

where $n$ is the order of reflection, which may be any integer (1, 2, 3, ...). The value of interplanar spacing at the peaks corresponding to (1 1 1), (2 0 0), (3 1 1) and (2 2 2) planes comes out to be 2.52 Å, 2.18 Å, 1.54 Å, 1.31 Å and 1.21 Å respectively. Average size of SiC nanocrystals before and after PVA grafting was calculated using equation (2) from the major peak corresponding to (1 1 1) plane. The size obtained for as received SiC nanocrystals is about 37.5 nm which is found to be increased to ~40 nm after the grafting of PVA on SiC nanocrystals. This increase in the average size of SiC nanocrystals suggests the presence of PVA on its surface. This fact supports the results obtained from FTIR and Raman spectroscopy.

Figure 4 shows the TEM images of as received SiC nanocrystals and PVA-g-SiC nanocrystals. In the TEM image of PVA-g-SiC nanocrystals, SiC appears dark, while PVA appears bright. From the image uniform coating of PVA on the SiC nanocrystals has been observed. Morphological verification was further carried out using SEM. Figures 5(a) and (b) shows the SEM images of as received SiC nanocrystals and PVA-g-SiC nanocrystals respectively. SEM images clearly show a uniform distribution of PVA over the SiC nanocrystals. Hence, both TEM and SEM micrographs points towards the change in the morphology of as received SiC nanocrystals.

Due to the organic coating around the inorganic nanofiller particles, the thermal performance of the nanofillers gets affected. The evaluation of the thermal performance of surface modified nanofillers is essential as it significantly affects the final properties of the material. The modified nanofillers with inferior thermal performance would not be suitable for high temperature processing as well as applications. The thermal response of PVA-g-SiC nanocrystals was analyzed using Thermo gravimetric analysis (TGA) and the degree of PVA grafted onto the surface of SiC nanocrystals was obtained.

Figure 6 shows the TGA curve for as received SiC nanocrystals and PVA-g-SiC nanocrystals. From the figure it can be seen that TGA shows a slight weight loss at 100 °C for as received SiC nanocrystals, which was assigned to the loss of water. After approximately 100 °C, main oxidation process started which resulted in the increase in weight [31] and the weight loss began at approximately 620 °C in air and is attributed to the oxidation of carbon [32]. However, the thermal degradation of PVA-g-SiC nanocrystals is entirely different from that of as received SiC nanocrystals. The thermal degradation of PVA-g-SiC nanocrystals consists of two stages of degradation. In the first stage, TGA shows initial weight loss upto 100 °C which is same as that obtained for as received SiC nanocrystals and is attributed to the loss of water. However, in the second stage from ~141 °C to 413 °C the major weight loss takes place. This loss could be caused by the thermal degradation of the grafted polymer onto the surface of SiC nanocrystals. The grafting degree is highly dependent on the initial quantity of polymer used and the reaction time [33]. On comparison of the thermal degradation processes of as received SiC nanocrystals and PVA-g-SiC nanocrystals, it can also be deduced that the amount of PVA grafted onto the surface of SiC is very small. The total amount of the grafted component is about 1.2% (calculated using equation (1)). However, the formation of active sites on SiC nanocrystals surface and hence grafting with PVA is confirmed.
4. Conclusions

PVA was successfully grafted onto the surface of SiC nanocrystals using a novel technique. The vindication of the grafting procedure has been done using FTIR spectroscopy, Raman spectroscopy, XRD, TEM and SEM. TGA studies revealed that the amount of PVA grafted onto the surface of SiC nanocrystals depends on the initial amount of PVA used. FTIR and Raman spectroscopy confirmed the attachment of PVA onto the surface of SiC nanocrystals by introducing various functional groups. \( I_D/I_G \) ratio is also a good indicator of the degree of grafting; an increase in this ratio implies that more desired groups are bonded onto the surface of SiC nanocrystals. From XRD measurements the size of PVA-g-SiC nanocrystals is found to be higher than that of as-received SiC nanocrystals calculated using Scherer’s equation, thereby confirming the presence of PVA onto the surface of SiC nanocrystals. XRD analysis further confirmed that the crystalline geometry of SiC nanocrystals is not altered by grafting procedure.

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