The effect of AlOOH boehmite nanorods on mechanical property of hybrid composite coatings

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ABSTRACT

AlOOH boehmite nanorods were used as a filler to develop sol gel based and polymer based hybrid composite coatings. The fracture toughness of the composite coatings was significantly improved by the nanorods as supported by nanoindentation test on sol gel based coatings and buckling test on polymer based coatings. The better fracture toughness of the nanorod filled composite than the conventional composite can be explained by the high aspect ratio of rigid nanorods, the orientation of nanorods along surface direction observed in the composite coatings, as well as chemical affinity between nanofillers and the matrix after they reacted with organosilane.

1. Introduction

One-dimensional (1-D) nanorods and nanofibers of boehmite (AlOOH) are of significance for use in advanced catalysts, adsorbents, composite materials and ceramics [1–3]. Numerous studies on boehmite nanofibers have been undertaken in recent years [4–6] and low temperature methods have been developed for growth of nanorods and nanowires without using of template, through solution-based processes. We have previously reported a procedure for steam-assisted, solid phase conversion of amorphous aluminum hydroxide wet-gel to well-crystallized 1-D nanostructure of boehmite AlOOH nanorods without using surfactants or solvents [7]. The process is unique for its simplicity, high efficiency of crystal growth and its potential to be operated at a large scale.

It is well known that composites loaded with fillers of high aspect ratio can offer reinforcement to the matrix at lower filler concentrations than the conventional spherical shaped fillers [8]. This advantage has significant implications since lower filler levels translate into lighter components as well as lower cost, which is desirable in many applications. The effect of nanofillers with higher aspect ratio on polymeric composites has been extensively investigated theoretically [9,10] and experimentally with the rise in research interest in nanocomposites [11–13].

The objective of present research is to investigate the effect of boehmite nanorod on mechanical properties of sol gel based and polyurethane (PU) based hybrid coatings since both systems have great significance in development of transparent protective coating for a wide variety of applications.

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2. Experimental procedure

To prepare the sol gel composite coating, an appropriate amount (up to 40 wt.% in final coating) of boehmit nanorod water dispersion was slowly added into hydrolyzed 3-glycidoxypropyltrimethoxysilane (GPTS) (Dynasylan GLYMO, Degussa) under intensive stirring for 72 h before coating. For the purpose of comparison, the same amount of boehmite nanoparticle (DISPAL 23N4, Sasol Geramny GmbH) was used as a filler in a separate experiment. Sol gel coatings were deposited on glass substrate by spin coating and dip coating process then thermally cured. Details of sample preparation can be found in [14].

In preparation of polymer composite coating, an appropriate amount (5 wt.% in final coating) of bohemite nanorods was first reacted with GPTS under the aforedescribed condition then separated with excessive GPTS by centrifuge and washed by methylpropanol repeatedly. The gathered boehmite powder was dispersed into solution of UV curable urethane oligomer (Addison Clear Wave (Wood Dale, IL USA)) diluted by methylpropanol at a 50:50 ratio and mixed by a high shear mixer (Silverson L4RT) to get a stable coating solution. The coating solution was applied on plastic substrates (PMMA and PC plate and compliant sheet) by bar coating or applicator coating. For buckling test, polycarbonate sheets with a thickness of 250 µm were used as substrate. All coating samples were cured by a medium pressure Mercury Fusion UV system. Both sol gel based and polymer based coatings obtained according to above described process were transparent and had excellent visual quality.

Field emission scanning electron microscope (FESEM) photos of samples were taken by JEOL JSM-6340F. High-resolution transmission electron microscopic (HRTEM) images were taken by a TECNAI F20 (G^2) (FEI) electron microscope operated at 125 kV. Nanoindentation tests were performed on a NanoTest 550 nanoindentor with a three-edged Berkovich diamond tip as indenter. Fourier transform infrared (FTIR) spectra of boehmite samples were obtained by a Bio-RAD (Excalibur Series) IR spectrometer scanning on KBr pellet samples.

In order to test the fracture toughness of polymer composite coating on compliant substrates, a controlled buckling test was conducted on a fixture described elsewhere [15]. The test was done on the prepared strips of substrate with coating on up side and clamped on both ends as depicted in Fig. 1a so that a higher strain could be achieved through buckling. One end of the clamp was fixed in position whereas the other end was used to slowly introduce the displacement manually. Through this buckling, the film which was placed on the convex side under buckling experienced a uniaxial tensile loading and was stretched to the point of cracking. This cracking process was observed under a light microscope, as shown in Fig. 1b is such a buckled sample after being released from the fixture. Through a large deflection solution for the radius of curvature under buckling [16], we can obtain the radius of bending curvature by inputting the measured displacement as an indication of the steady-state cracking through film thickness [17,18]. From all the above, the fracture toughness, which is indicated by the critical energy release rate, can be determined after the critical strain in the film is calculated from the lateral buckling displacement. Theoretical details of this test and its applications can be found in the listed references especially Refs. [15] and [18]. The modulus used for calculating film plane strain was obtained from the nanoindentation test.

3. Results and discussion

Fig. 2 is a TEM picture of the as-synthesized nanorods showing the typical morphology of this material. The picture clearly shows that the rods have good uniformity, with lengths of 200-300 nm and diameters of 10-20 nm. XRD patterns of the boehmite nanorods and of Dispal nanoparticles exhibited a well-defined XRD pattern indexed to the boehmite AlOOH [7,14] indicating that the fillers were free from other contaminations. Based on the XRD spectra and the TEM evidence for both boehmite AlOOH nanomaterials (the TEM of Dispal nanoparticles can be found at http://www.sasol.com), it is assumed that both nanofillers have similar physical properties, thus the only difference between them is their geometric shape.

Fig. 3 shows a top view of the 40 wt.% filled spin coating sample taken by FESEM. The nanorods are homogenously spread across the substrate and are oriented along the surface direction. This is due to the fact that during the spin coating process, fillers in the coating dispersion were spread under the centripetal flow force along the surface direction and once settled they had no time to change their orientation due to the fast evaporation of solvent that solidified the film. Similar distribution morphology was also found in sol gel dip coat samples and PU based coatings which can be explained by the same reason though flow force and solvent evaporation speed were lower than in the case of spin coating.

It is well known that the nature of the matrix/reinforcement interface plays a very important role in determining the mechanical properties of a composite especially in the case of a nanocomposite, when filler size is on a nanometer scale, which takes up a large specific area in a composite. To investigate the interaction of boehmite nanofillers with their host matrix at the interface, FTIR and zeta potential measurements were undertaken on both as-received boehmite nanofillers and on the same material after reacting with GPTS. The latter nanofillers were separated from excessive GPTS and solvents by repeatedly centrifuging and washing with deionized water and ethanol. Zeta potential measurement results of both nanorods and nanoparticles showed the same trend after reacting with GPTS, namely the isoelectric point (IEP) of both fillers shifted to a lower pH, which indicated a surface interaction between GPTS and the boehmite nanofiller due to the sol gel reaction [14]. Fig. 4 shows the FTIR spectrum of the boehmite nanorod before and after reacting with GPTS. For the nanorods of boehmite AlOOH, five strong absorbance bands (486, 660, 761,1074 and 1163 cm^{-}1) can be observed indicating the asymmetric stretching, angle bending and angle deformation (wagging) of (OH) – Al = O respectively [7]. A sharp band that occurred at 1384 cm^{-}1 came from the vibration overtone of surface OH groups [19]. After reacting with GPTS, the surface of the nanorod was modified by a layer of organosilica as a product of sol gel reaction which can be identified by spectrum (b) in Fig. 4. Peaks at 2940 and 2872 cm^{-}1 correspond to the symmetric and asymmetric stretching vibration of C - H from the organic component of GPTS while the disappearance of the peak at 2842 corresponding to -O- C_xH_y suggests the completeness of the sol gel reaction. The broadened peak between 1000–1200 cm^{-}1, compares to the two clear sharp peaks at 1074 and 1063 cm^{-}1 in spectrum (a), which is possibly due to the overlapping of Al - O - Si, Si - O - Si and C- O - Si bonding formed in the sol gel reaction. The intensity of the above peaks representing organosilica suggests that the amount of sol gel product on the filler surface is more than a molecular layer.

Reactions between oxide particles and silane coupling agents have been investigated extensively [20,21]. In the present case, the GPTS as an organotrialkoxysilane modified the boehmite particle surface due to its ability to readily undergo hydrolysis and condensation reactions on the hydrophilic surface of the nanofiller. By grafting of nonhydrolyzable epoxy functionality onto the surface, while the remaining silanol groups were screened along particle surface, an additional steric repulsive force among nanofillers developed between the suspended filler particles. Such surface modification provided greater stability against particle agglomeration and a compatible interface between particles and the sol gel matrix. The organosilane modified surface also led to a compatible interface between boehmite filler and PU oligomer/solvent system thus the coating solution was also stable. Since filler-matrix adhesion is governed by chemical and physical interactions at the interface, such functionalization is considered responsible for improving mechanical properties in nanofiller-reinforced composites, by increasing the stress transfer between matrix and nanofillers in the composite. Given the orientation of nanorods in, it is obvious that such filler/matrix bonding would be beneficial more to the enhancement along surface direction.

Modulus and hardness value of sol gel coatings were obtained by the nanoindentation test.

In the present research, a layer of 2 µm sol gel coating, with a 40 wt.% boehmite filler, was obtained on the glass substrate according to the aforedescribed coating process. Indentation results obtained at a maximum depth of 200 nm were used to report the mechanical properties of these samples. Modulus and hardness values obtained for the nanoparticle filled material were 9.88±0.5 GPa (measurement standard error) and 0.98±0.06 GPa respectively. For nanorod filled samples these values were 8.86±0.7 GPa and 0.83±0.04 GPa. The lower values for nanorod filled coatings could be attributed to the orientation of the nanorods since nanorods in the composite were observed to be horizontally oriented and thus provide less support to the force applied from direction normal to the surface, while in the nanoparticle filled coating, the isotropic distribution of the rigid filler may offer more support under compression.

It was observed that cracking, delamination and chipping occurred during indentation loading on sol gel coatings on glass substrates which allow a qualitative determination of fracture toughness [22]. Fig. 5a and b are the indents made on nanorod filled and nanoparticle filled coatings under a load of 490 mN, which was the upper limit of our nanoindentor. They show significant different deformation morphologies. As shown in Fig. 5a, chipping of the coating was in the form of a segment of a disk, in response to the in-plane compressive stress. Such fracture feature is described as a result of secondary radial cracks emanating from the vicinity to edges of the contact impression [23]. Compared with the extensive chipping observed for the nanoparticle filled coating, the nanorod filled coating exhibited a much smaller scale of cracks and a different pattern of fracture damage. As shown in Fig. 5b, though slight delamination was observed, as indicated by the optical interference stripes, there was no sign of chipping. Rather than extensive cracks emanating along, or at an angle to the indenter's edges as observed in nanoparticle filled coating, some lighter radial cracks in the nanorod filled sample were found between contact edges, accompanied by tiny cracks perpendicular to such radial cracks (as indicated by the arrows). Such features were considered to be due to the release of indent pressure in the film as the indenter was removed, which allowed relaxation of large deformation resulting from coating layer's buckling under indentation. In spite of the cracks that were found at the contact edge between coating surface and the edges of indenter. These cracks may happen during unloading therefore no crack event was recorded. It is clear that the above observations implied a significantly higher crack toughness in the nanorod filled coating.

The crack toughness of PU composite coatings was tested by a controlled buckling test. During the buckling, the displacement was applied slowly to detect the first moment when the crack just started to appear. When the crack first formed, the displacement was recorded for toughness calculations. It was also observed that once the crack started to form, it propagated through the whole width of the strip rapidly. There were also simultaneous cracks parallel to one another occurring. The microscope photo in Fig. 1b was taken after the buckling to illustrate this occurrence. The adhesion test of all PU coatings on polymer substrates according to ASTM-D3359 gave a 5B result which means that the adhesion between the coating and the substrate was quite good thus the cracks originated and grew in the coating layer during the buckling test.

Three types of composite samples namely pure PU coating, 5 wt.% nanoparticle filled coating and 5 wt.% nanorod filled coating were tested by the buckling test. Five pieces of each type of sample were tested and the average toughness values with their standard deviations are tabulated in Table 1. The modulus listed here was obtained by the indentation test on coating samples applied on the glass substrate with the maximum indent depth within one tenth of the coating thickness. As shown in Table 1, the modulus of the nanoparticle filled sample is slightly higher than that of the nanorod filled sample. This is consistent with the result obtained from sol gel based samples. Looking at the toughness values from the table, the nanorod filled coating doubled that of the control sample and also the nanoparticle filled system had a slightly higher toughness than the control sample. The above results clearly show the better fracture toughness of the coating with nanorods as rigid fillers. The improvement also coincided with the findings in indentation on sol gel coatings which derived the better fracture toughness through the cracking profile of the film under nanoindentation.

A reasonable explanation for such crack toughness improvement in both sol gel based and PU based composite coatings is that due to the higher aspect ratio, nanorods tend to form a cross-ply structure in the composite that retarded the growth of cracks, and thus enhanced their crack toughness. The observed orientation of nanorods in the composite coating suggests that such enhancement was induced mainly along the direction of the surface and resulted in better enhancement of crack toughness along the surface direction (radial crack under indentation and parallel crack under buckling). Combined with the slightly lower measured values of modulus and hardness, it appears that the nanorods may be better able to bear flexural load, when compared with the nanoparticle filled composite, which can only be compressed. Also the surface modification by organosilane helped to improve the dispersion of the nanofiller in the composite and an organophilic interface helped the load transfer under indentation and tensile stress.

4. Conclusions

AlOOH boehmite nanorod filled sol gel based and polyurethane based composite coatings can be obtained on different substrates with good quality. A compatible interface between nanofillers and matrix material was found after fillers reacted with GPTS. The modulus and hardness of nanorod filled coating were slightly lower than those of the same composite coating filled with nanoparticles while their crack toughness was significantly improved as supported by the nanoidentation test on sol gel coatings and the buckling test on polymer composite coatings. The toughness improvement brought by nanorods can be attributed to firstly their higher aspect ratio which made nanorods tend to form a cross-ply network in the composite which retarded the growth of fractures; secondly the orientation of nanorods in composite coatings led to better enhancement along the surface direction and finally chemical affinity between nanofillers and matrix after their surface was modified by GPTS.

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List of Tables

Table. 1 Tabulation of measurements for fracture toughness calculation

List of Figures

Figure. 1 Controlled buckling test and the observed cracks (a) buckling of strip sample with on end fixed and another end free. (b) Cracks (indicated by arrows) of the buckled PU coating after being released from buckling.

Figure. 2 The TEM of obtained boehmite nanorods.

Figure. 3 SEM micrograph of 40 wt.% nanorod filled coating deposited by spin coating showing orientation of the nanorods in the composite coating.

Figure. 4 FTIR spectra of boehmite nanoroads before (a) and after (b) reacting with GPTS.

Figure. 5 Indents made on coating samples by maximum 490 mN load (a) nanoparticle filled coating (b) nanorod filled coating.

Coating film	Film thickness (μm)	$\overline{E}_f$ (GPa)	Toughness (J/m^2)
Pure PU	3.7	8.98	27.79±1.43
5 wt.% Boehmite nanoparticle filled	3.5	9.43	33.08±1.35
5 wt.% Boehmite nanorod filled	3.2	9.22	56.28±2.62

Table 1

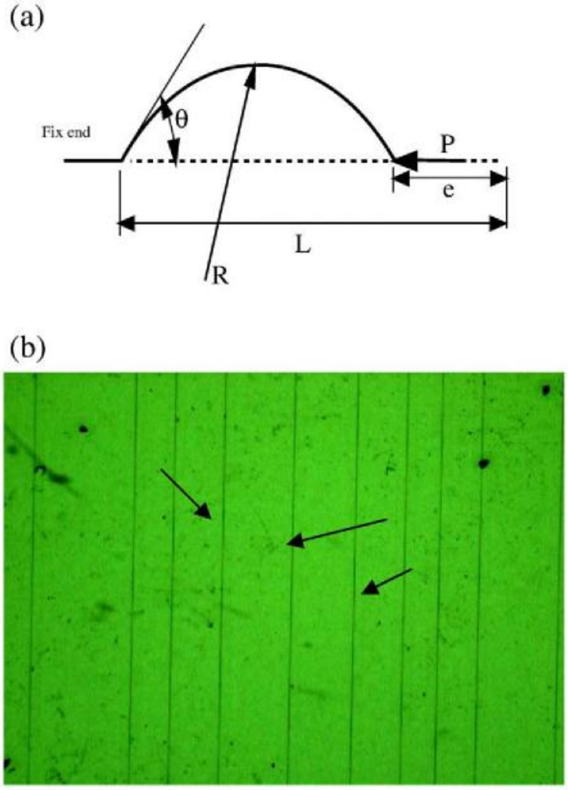


Figure 1

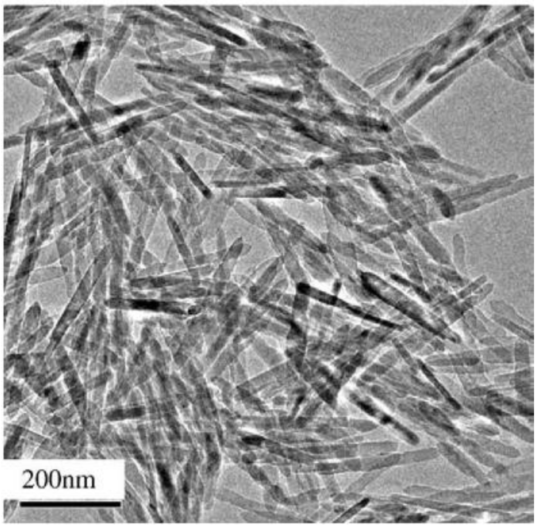
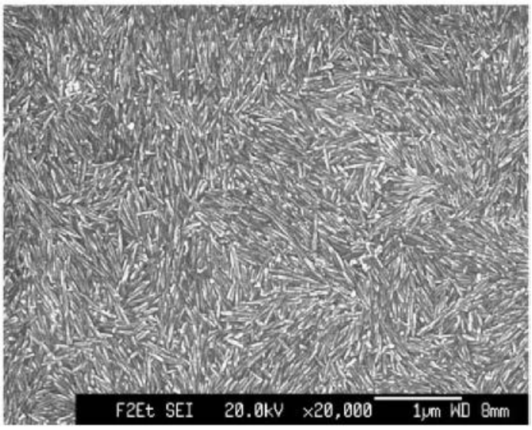


Figure 2



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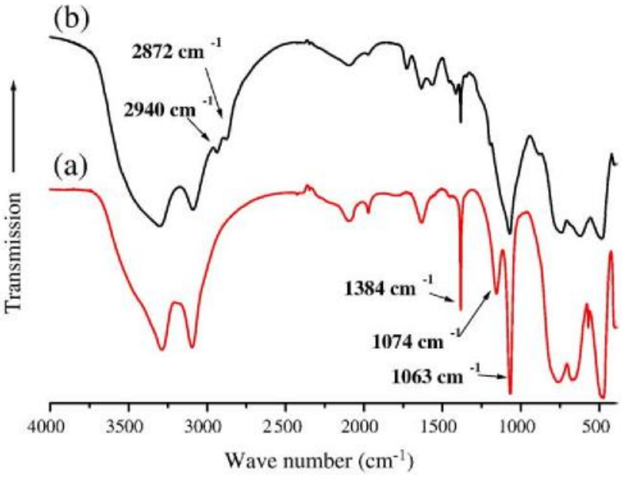
(b)
(a)
2872 cm -1
2940 cm -1
1384 cm -1
1074 cm -1
1063 cm -1
Transmission
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3500
3000
2500
2000
1500
1000
500
Wave number (cm-1)

Figure 4

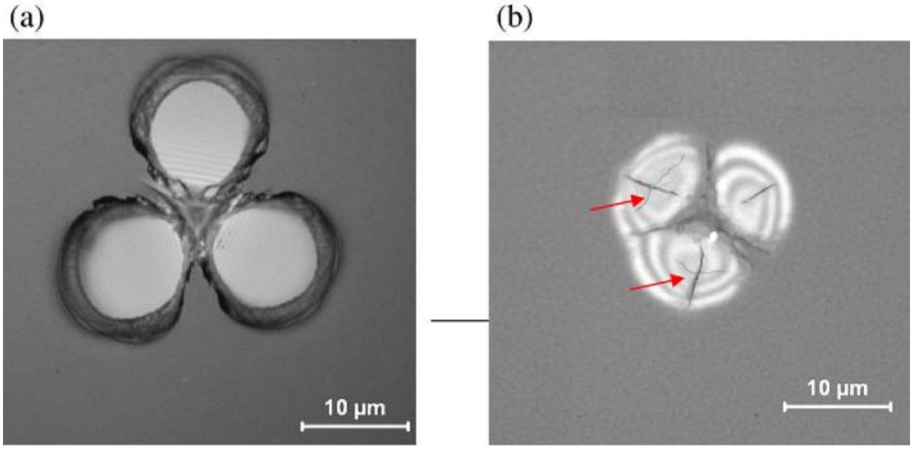

Figure 5