

Effects of Polyhedral Oligomeric Silsesquioxane Coatings on the Interface and Impact Properties of Carbon-Fiber/Polyarylacetylene Composites

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ABSTRACT: Two kinds of polyhedral oligomeric silsesquioxane (POSS) coatings were used for the modification of the interface in carbon fiber (CF) reinforced polyarylacetylene (PAA) matrix composites. The effects of the organic-inorganic hybrid POSS coatings on the properties of the composites were studied with short-beam-bending, microdebonding, and impact tests. The interlaminar shear strength and interfacial shear strength showed that the POSS coatings resulted in an interfacial property improvement for the CF/PAA composites in comparison with the untreated ones. The impact-test results implied that the impact properties of the POSS-coating-treated composites

were improved. The stiffness of the interface created by the POSS coatings was larger than that of the fiber and matrix in the CF/PAA composites according to the force-modulation-mode atomic force microscopy test results. The rigid POSS interlayer in the composites enhanced the interfacial mechanical properties with a simultaneous improvement of the impact properties; this was an interesting phenomenon in the composite-interface modification. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5202–5211, 2006

Key words: adhesion; coatings; composites; impact resistant; interfaces

INTRODUCTION

It is well known that the interface between the fiber and matrix plays a significant role in controlling the overall properties of fiber-reinforced polymer composites.¹ Good fiber-matrix adhesion is important in achieving efficient stress transfer from the matrix to the fiber. However, in general, an improvement in the fiber-matrix interfacial shear strength (IFSS) leads to a reduction of the composite toughness. The efficiency of the fiber-matrix stress transfer depends on the chemical compatibility of the constituents and is also affected by the ratio of the Young's modulus or stiffness of the fiber and the matrix. Theoretical analysis² has suggested the influence of the interfacial layer on the composite properties and speculated that, with the proper selection of the polymer in the interfacial region, a good combination of tensile and impact properties could be achieved. In fact, an efficient approach to optimizing the stress-transfer efficiency and impact toughness is to modify the

interface via the coating of the fiber with a polymer/copolymer, which contributes to the toughness of the composite. The efficiency of improving IFSS without a loss in the impact properties by an interlayer has been demonstrated with different flexible polymeric interlayers.^{3–7} However, several organic-inorganic hybrid coatings on fibers result in a rigid interface, and this is considered to be disadvantageous to the impact properties of composites. Therefore, the drawback of a rigid interface for the impact performance of composites is assumed as a matter of course without the study of materials in detail to determine whether it is always true or not.

Polyarylacetylene (PAA), a candidate for the matrix of the next generation of high-temperature composites, has been investigated because of its outstanding heat resistance and excellent ablative properties.⁸ PAA is a high-performance resin made of nonpolar, structural, ethynyl, aromatic hydrocarbons that can be cured into a highly crosslinked, aromatic polymer that contains only carbon and hydrogen by means of addition polymerization without any elimination of small molecules such as water or gas. PAA has advantages over other state-of-the-art phenolic resin systems because of its ease of processability, smaller hygroscopic coefficient, lower pyrolysis shrinkage, and higher char yield.⁹ The prepolymer of PAA is either a low-viscosity liquid or a low-melting solid, which is easily fusible at a low temperature, so it is convenient for the contour machining of

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composites by conventional curing processes with low or middle pressure.¹⁰ The main reason for investigating PAA, which is used as a matrix resin for heat-resistant composites in spacecraft structural materials, is its low absorption of water. The hygroscopic coefficient of PAA is 0.1–0.2%, which is 1/50 of that of a phenolic resin. The volatilizable component in the PAA resin is only 10 mass %, which is much less than that of a phenolic resin (>40 mass %) when the polymer is heated to high temperatures in an inert environment. Theoretically, the char yield of the PAA resin can reach approximately 90 mass %, which implies that a slight amount of the volatile product and minimal shrinkage are associated with its pyrolysis.

The nature of the structure and the chemical inertia of the carbon fiber (CF) and the nonpolar structure of PAA result in weak bonding in CF/PAA composites. Thus, the prospective performance of CF/PAA composites dependent on perfect adhesion can hardly be accomplished. The weak adhesion means that the composites quickly lose their advanced properties when they are used as thermal protection materials, which are ablated by high temperatures and high-speed gases. Hence, the outstanding heat resistance and excellent ablative properties of PAA cannot be materialized. It is necessary to improve the interfacial performance of CF/PAA composites.

In this work, to obtain more ideal interfacial properties for the composites, organic–inorganic hybrid nanomaterials with excellent heat resistance, that is, polyhedral oligomeric silsesquioxane [POSS or $(\text{RSiO}_{1.5})_n$, where $n = 6, 8, 10, \dots$] materials, were introduced and used as coatings on CF surfaces. POSS refers to one kind of compound that contains a silicon–oxygen nanostructural skeleton with intermittent siloxane chains of the general formula $\text{RSiO}_{1.5}$, R being hydrogen, alkyl, alkylene, aryl, aromatic alkylene, or their derivative groups,¹¹ which are active or inertial functional groups. POSS can be prepared through the hydrolytic condensation of the organic siloxane $\text{RSi}(\text{OR}')_3$, R and R' being the different organic groups of the precursor.¹² Numerous publications concerning the development and incorporation of dispersed POSS into traditional organic polymer systems have been published, and the number of them increases year by year. This research has resulted in a new generation of hybrid inorganic–organic polymer systems with remarkable enhancements in the mechanical and physical properties, including dramatic increases in both glass-transition and decomposition temperatures,^{13,14} reduced flammability,¹⁵ increased modulus,^{16,17} and oxidation resistance.^{18,19} POSS with appropriate functional groups, including active vinyl group or inertial groups, was used in different CF surface coatings in this study. The effects of POSS-coating treatments of the fiber surface on the interface and impact properties of CF/PAA composites were investigated.

EXPERIMENTAL

Materials

The PAA resin used for the fabrication of the composite specimens was supplied by the Aerospace Research Institute of Material and Processing Technology (Beijing, China). Polyacrylonitrile precursor CFs (3K), with a typical value of 3.38 GPa for the tensile strength, were obtained from Jilin Carbon Co. (Jilin, China). There were two different kinds of POSS: methacrylisobutyl-POSS and trisilanolphenyl-POSS. Their structures are shown in Figure 1, and they were applied as coatings to treat the surfaces of CFs. Both POSS compounds were bought from Hybrid Plastics Co., Inc. (Texas), and were used as received. Analytically pure acetone and tetrahydrofuran (THF) were purchased from the First Factory of Chemical Agents (Tianjin, China). Epoxy resin (E-51; molecular weight = 350–400) was obtained from Xingchen Chemical Wuxi Resin Factory (Wuxi, China). Phenol resin (barium phenol resin) was also supplied by the Aerospace Research Institute of Material and Processing Technology.

Methods

CF surface-coating treatments and preparation of the CF/PAA composites

CFs were extracted with acetone for 12 h to clean the fiber surface and dried at 80°C for 3 h before the treatment with POSS coatings. THF solutions of POSS with different concentrations (1, 2, and 3 mass %) were prepared for the coatings. CFs were immersed in the prepared solution for 2 h to coat POSS onto the fiber surface, and then the fiber was dried at 80°C for 3 h. The unidirectional and long CF-reinforced PAA composites were made with both untreated and coating-treated CFs. CF was wound on a square hob. Thus, a small axial tensile force was applied to control the fiber direction in the mold. Curing was performed in a compression-molding machine by compression molding. The content of the resin in the composites was controlled to be about 35 mass %. The curing process was 120°C for 2 h, 140°C for 2 h, 180°C for 2 h, 200°C for 2 h, and 250°C for 0.5 h. During the curing process, the pressure was 2 MPa, which was loaded after the temperature was increased to 120°C. After the curing process was finished, the mold was cooled to room temperature, with the pressure being maintained. All composite samples were approximately 200 mm long, 6 mm wide, and 2 mm thick.

Interfacial characterization of the CF/PAA composites

The short-beam bending test of the CF/PAA composites was carried out on a universal testing machine

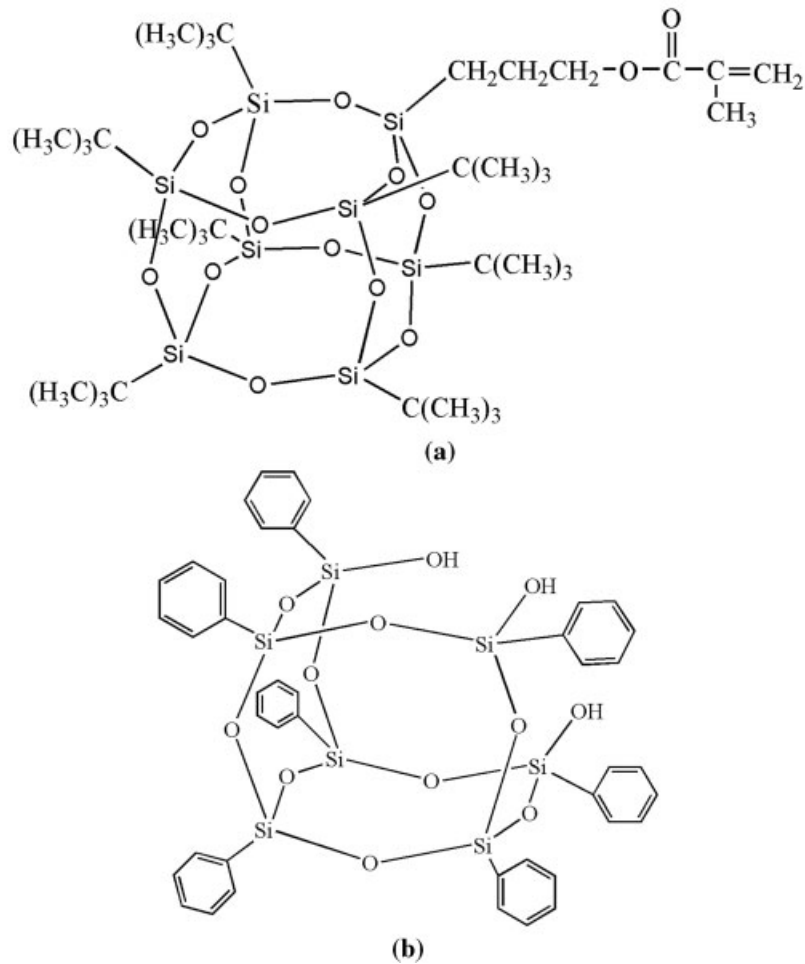


Figure 1 Structures of different POSS coatings: (a) methacrylisobutyl-POSS and (b) trisilanolphenyl-POSS.

(WD-1, Changchun Second Material Experiment Factory, Changchun, China) with a three-point short-beam-bending test method according to ASTM D 2344. The specimen dimensions were 20 mm × 6 mm × 2 mm, with a span-to-thickness ratio of 5. The specimens and the enclosed space in which the test was conducted were maintained at room temperature. The specimens were tested at a rate of crosshead movement of 2 mm/min. The interlaminar shear strength (ILSS or Γ) for the short-beam test was calculated according to the following equation:

$$\Gamma = \frac{3P_b}{4bh} \quad (1)$$

where P_b is the maximum compression load at fracture (N), b is the breadth of the specimen (mm), and h is the thickness of the specimen (mm). Each reported ILSS value was the average of more than eight successful measurements.

Microdebonding testing of the composites was conducted at room temperature on an *in situ* interfacial strength testing instrument (HIT-300, Harbin Institute

of Technology, Harbin, China) according to ASTM STP 893. As shown in Figure 2(a), the specimen (3 mm long, 6 mm wide, and 2 mm thick) was cut from the unidirectional composites (perpendicularly to the direction of the CFs). The cross section of each specimen was polished with conventional metallographic techniques so that it could be observed clearly under the microscope. During the experiment, a single fiber was selected, and a diamond microprobe was used to push axially against the end of the fiber, with a loading speed of 0.01 $\mu\text{m/s}$, until interfacial debonding occurred (shown in Fig. 2). The force value and the debonding extent were recorded during tests. Linear function $F(x)$ between load f and debonding extent x , that is, $f = F(x)$, could be determined on the basis of the test data. Then, the force value at just debonding was obtained according to the determined function. More than 40 fibers were chosen for testing to obtain the function in each specimen. The force value at just debonding was input into a finite element analysis program, with which the force value could be changed into IFSS according to a hexagonal array model of fibers in three-dimensional composites.

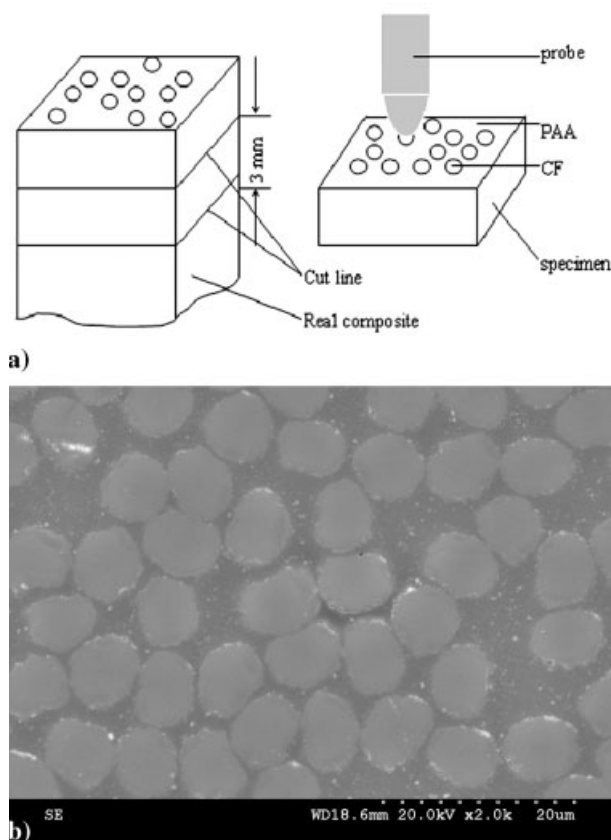


Figure 2 (a) Sketch of microdebonding tests and (b) CF/PAA composite cross section.

Impact properties of the CF/PAA composites

Nonstandard impact specimens 60 mm long, 6 mm wide, and 2 mm thick were tested on an instrumented Charpy system impact testing machine (CIEM-30D-CPC, Testing Machine Institute, Tokyo, Japan) that was designed and built specifically for this investigation. The specimens were unnotched. The impact span was 55 mm. After manipulation of the impact, a force–displacement trace during the impact of each specimen was recorded by the machine itself. The initiation impact resistance (initiation energy absorbed before the peak failure of the specimen), the propagation impact resistance (propagation energy absorbed after the peak failure of the impact specimen), and the total impact resistance were obtained with numerical integration techniques. Each reported value was the average of at least four successful measurements.

Atomic force microscopy (AFM) force-modulation-mode test

The unidirectional CF/PAA composites with lengths greater than 4 mm were cut. The cross sections of the samples were washed with acetone after being

polished. The polish program was similar to that in the microdebonding test. AFM experiments were carried out on a Solver P47 AFM/STM system (NT-MDT Co., Mockla, Russia). The force modulation mode was adopted to study the cross-section surfaces of unidirectional CF/PAA composites and the relative stiffness of the various phases, including the CFs, interface, and resin. In the force modulation mode, the modulation of the contact force between the sample and the tip was achieved by the oscillation of the tip and the supporting base assembly through a piezoelectric bimorph that was built into a special tip holder. The line distribution of the relative stiffness of the CF/PAA cross-section surface, obtained from the statistical analysis of the relative stiffness image, was used to suggest the difference between POSS and conventional coatings.

Scanning electron microscopy (SEM) observation

An S570 scanning electron microscope (Hitachi Ltd., Tokyo, Japan) was used to observe the impact-fracture topography of CF/PAA composites. The samples were metalized into a thin layer of Pt (10 nm thick) and degassed before observation.

RESULTS AND DISCUSSION

Interfacial properties of the CF/PAA composites

The effect of the interface on the properties of a composite material depends on its quantity and characteristics.²⁰ In the case of the POSS-coating treatment on the fiber surface, the former depends on the concentration of the coating solutions and the immersion time, whereas the latter depends on the mechanism of interface formation and on the properties of each component. The interface was formed by physicochemical interactions of the composites in this study. Thus, the thickness of the interface was determined by the strength of the interaction, whereas the properties were determined by the characteristics of the components.

ILSS of the CF/PAA composites was calculated with eq. (1). The results of the experiments are shown in Figure 3, which indicates the effects of different POSS-coating solutions and different concentrations in the same coating on the ILSS of the CF/PAA composites. ILSS of the untreated CF/PAA composites was only 34.2 MPa, whereas ILSS of the untreated CF/epoxy resin and CF/phenolic resin composites was 64.3 and 46.8 MPa, respectively. Because of the inertial structure of CF and the nonpolar structure of PAA, ILSS of the untreated composites was small compared to that of epoxy and phenolic matrix composites. The low ILSS of the untreated CF/PAA composites showed that it was necessary to improve the interfacial mechanical

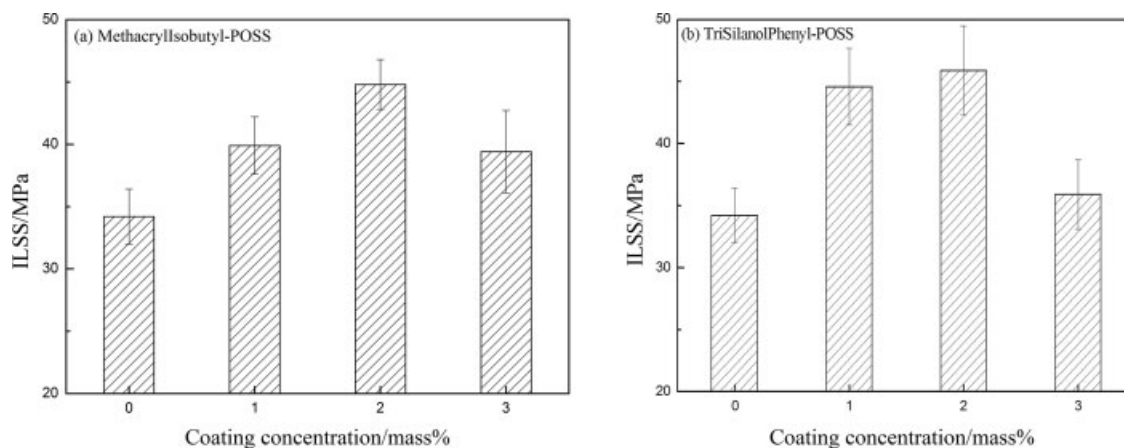


Figure 3 ILSS of untreated CF/PAA composites (the coating concentration was 0 mass %) and CF/PAA composites treated with different concentrations of (a) methacrylisobutyl-POSS and (b) trisilanophenyl-POSS coatings.

properties of the CF/PAA composites. ILSS was increased to a different extent after the CFs were treated with POSS coatings. ILSS increased with the increasing concentration of the POSS coatings and reached a peak when the concentration was 2 mass %. Then, ILSS decreased, but it still remained higher than that of the untreated composites. The interlayer could transfer energy from the matrix to the fiber when the composite was loaded, so the composite properties were improved. ILSS could be increased by 34% after CFs were modified by a 2 mass % trisilanophenyl-POSS-coating solution, whereas it was increased by 31% when CFs were treated with a 2 mass % methacrylisobutyl-POSS-coating solution. Comparing the ILSS values of the composites before and after the treatments with different coatings, we concluded that the different POSS coatings had almost the same treatment effects.

The same regularity appeared for IFSS of the composites that were treated with different coatings (shown in Fig. 4). IFSS of the untreated composites was 49.9 MPa because of the weak adhesion between the CF and PAA resin. IFSS was markedly increased by different degrees after CF was treated with POSS solutions of different concentrations. The maximum of IFSS appeared when the concentration was 2 mass %. IFSS of the CF/PAA composites treated with methacrylisobutyl-POSS was 63.6 MPa, increasing by 27% compared with that of the untreated composite. IFSS of the CF/PAA composites treated with the trisilanophenyl-POSS coating was 62.4 MPa, which was increased by 25% compared with that of the untreated composite. IFSS began to decrease when the concentration of the coating solutions continuously increased to 3 mass %. IFSS of the methacrylisobutyl-POSS-coating-treated CF/PAA composites was a little higher than that of the composites treated with the trisilanophenyl-POSS coating, whereas ILSS of the trisilanophenyl-POSS-coating-treated compo-

sites was higher than that of the composites treated with methacrylisobutyl-POSS. However, the differences in ILSS and IFSS of the composites treated with different coatings were so tiny that they could be ignored according to the results of the statistical analysis for the errors. Therefore, the functional groups on the cage structure of POSS had little effect on the interfacial mechanical properties of the CF/PAA composites. The cage nanostructure of POSS was the key factor that resulted in the improvement of ILSS and IFSS of the composites.

The values of ILSS and IFSS (as shown in Figs. 3 and 4) of the CF/PAA composites indicated that the POSS coatings had a remarkable effect on the interfacial properties of composites. Nearly identical results were obtained when the coatings were methacrylisobutyl-POSS and trisilanophenyl-POSS, even though there were different functional groups on the Si—O—Si cage framework. The cage structure of POSS effectively influenced energy transfer from the matrix to the fiber when the composites were loaded.

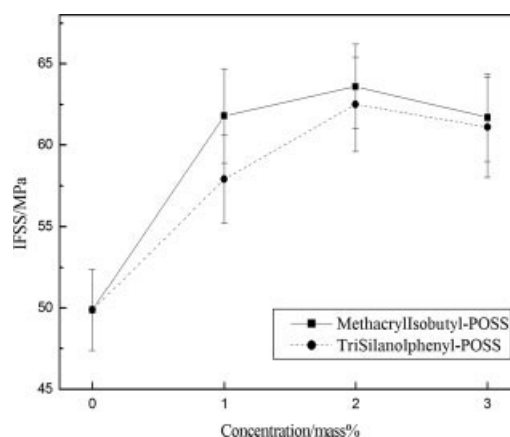


Figure 4 IFSS of CF/PAA composites modified with different concentrations of different coatings.

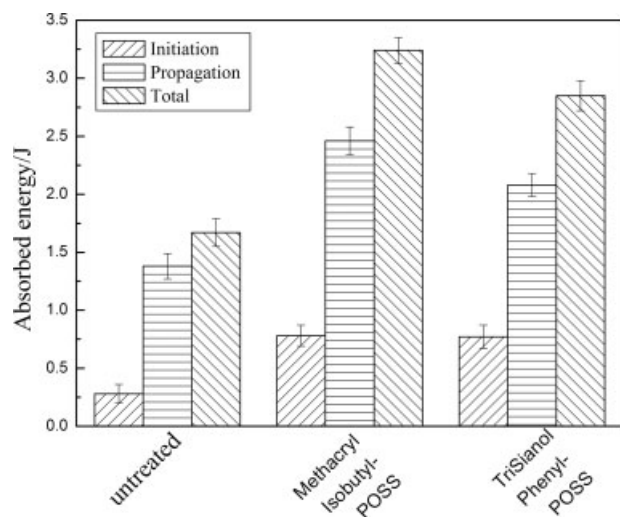


Figure 5 Impact properties of CF/PAA before and after treatment with different POSS coatings (the concentration of the coating solution was 2 mass %; initiation + propagation = total).

The groups on POSS might affect the interfacial properties of the composites. However, the conclusion that the cage structure of the POSS coating was the most important element could be drawn from these results.

Impact properties of the CF/PAA composites

The energy absorbed by the CF/PAA composites during the impact experiments is shown in Figure 5. The absorbed energy values could represent the impact resistance of the materials. The larger the absorbed energy was, the better the impact resistance was. Because of the brittleness of the PAA resin, the initiation, propagation, and total absorbed energies of the untreated CF/PAA composite were low (only 0.28, 1.38, and 1.67 J, respectively). After the surface of CF was treated with POSS coatings, all the types of absorbed energy were increased dramatically. Compared with those of the untreated composites, the initiation, propagation, and total absorbed energies of the CF/PAA composite treated with the methacrylisobutyl-POSS coating were increased by 179, 78, and 94%, respectively, and the initiation, propagation, and total absorbed energies of the CF/PAA composite treated with the trisilanolphenyl-POSS coating was increased by 175, 51, and 71%, respectively. The initiation absorbed energies of the CF/PAA composites treated with methacrylisobutyl-POSS and trisilanolphenyl-POSS were equivalent. The propagation absorbed energy of the CF/PAA composite treated with methacrylisobutyl-POSS was larger than that of the CF/PAA composite treated with trisilanolphenyl-POSS, and this could be caused by the functional groups on the cage structure. The

differences in the topographies of the samples after the impact tests (see Fig. 6) could illustrate that the POSS coatings increased the impact properties of the composites efficiently. There were more cracks in POSS-coating-treated CF/PAA composites than in the untreated ones (circles a–c in Fig. 6). The POSS cage nanostructure made the fracture of the treated composites more complex than that of the untreated ones. There were cracks at the end of the POSS-treated composites (circles e and f in Fig. 6), whereas no cracks were found at the end of untreated ones (circle d in Fig. 6). The cracks at the end were a clear indication that the fracture of the composites was strongly changed when the fibers were treated. The step indicated that the fracture changed from one dominated by normal (tensile/compressive) stresses to one dominated by a shear stress failure mode, which resulted from the POSS nanoparticles in the interfacial region of the composites. Figure 7 presents SEM images of different CF/PAA composite impact fractures. Figure 7(a) shows the tensile zone of the untreated composite fracture. There were different zones in the impact fracture, that is, a compression zone (not shown here) and a tensile zone. The fibers were pulled out because of the poor fiber–matrix adhesion. The adhesion between the fiber and resin was so weak that the pullout fiber surface was clean and the length was large. After the POSS-coating treatment, the differences in the tensile zone of the impact fracture were changed. The debonding between the fiber and matrix [Fig. 7(b,e)] and the pull-out fibers with the matrix [Fig. 7(c,d,f,g)] are shown.

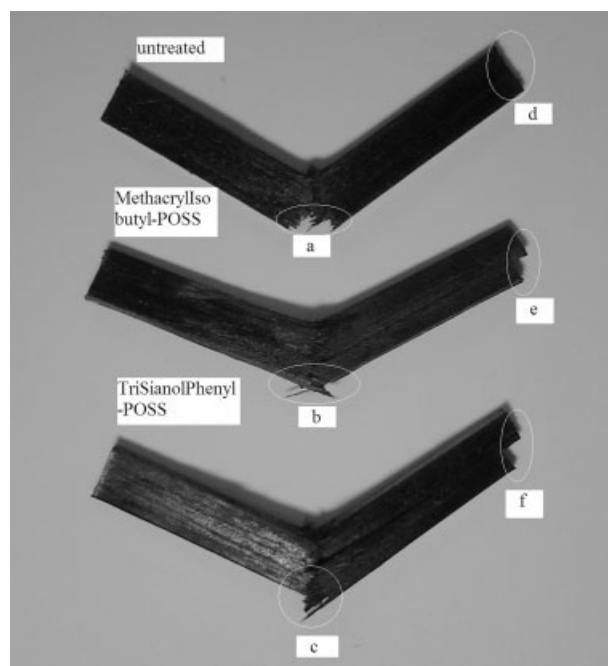


Figure 6 Samples with and without different POSS-coating treatments after impact testing.

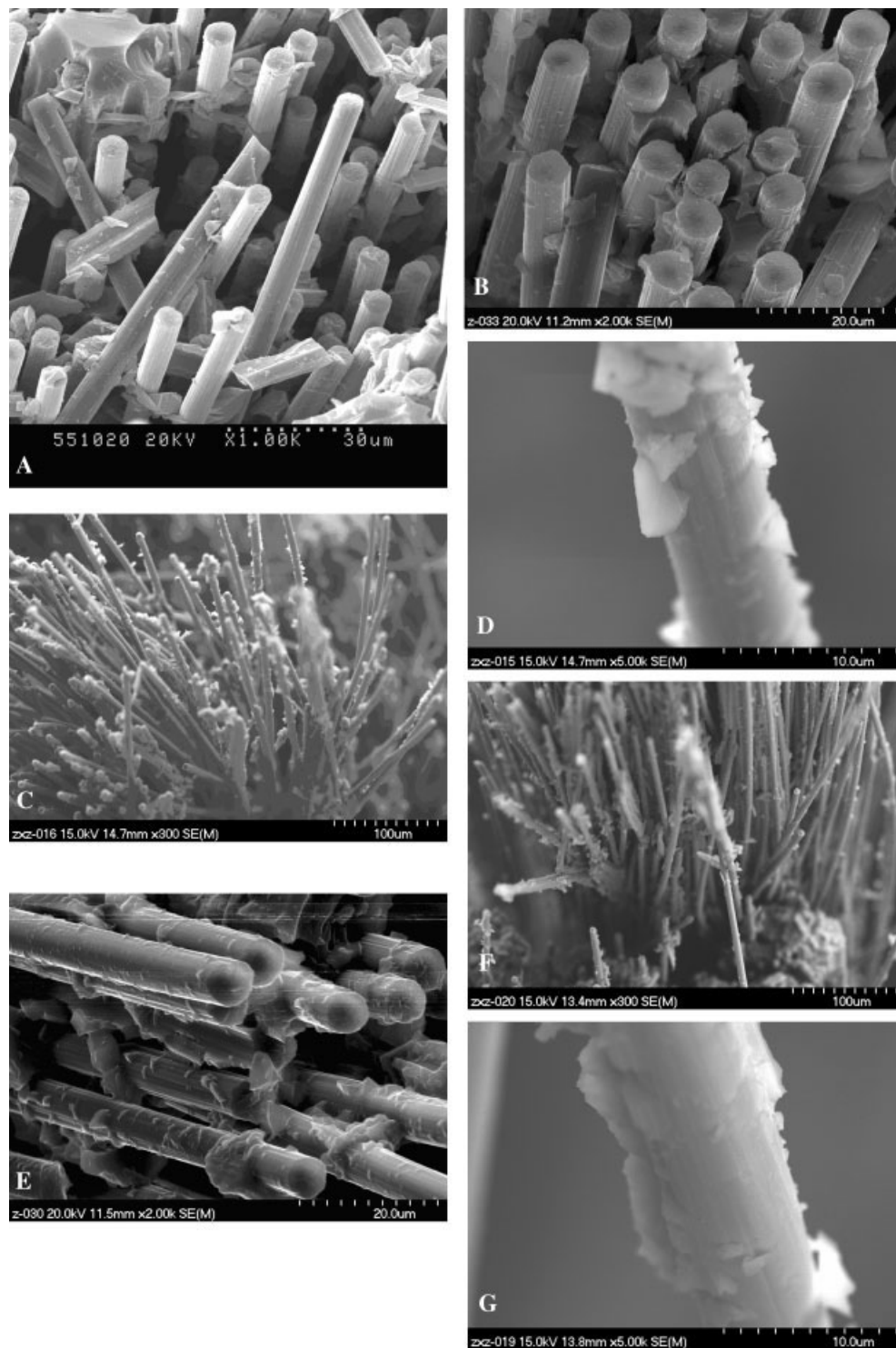


Figure 7 SEM morphology of CF/PAA composite impact fractures: (a) the untreated composite fracture, (b–d) different sections of the fracture in the composite treated with methacrylisobutyl-POSS, and (e–g) different sections of the fracture in the composite treated with trisilanolphenyl-POSS.

Figure 7(c,d,f,g)] indicates that there was resin on the pullout fiber surface, and this suggested good adhesion between the fibers and matrix. The length of the pullout fiber became small, and the quantity of the resin on the fiber surface was more than that on the untreated one.

The efficiency of importing an interlayer between the fibers and matrix in improving IFSS, without a loss of impact properties, was previously demonstrated^{21–23} with different interlayers. However, almost all the interlayers were soft or flexible. The modulus or stiffness of the interface was larger than

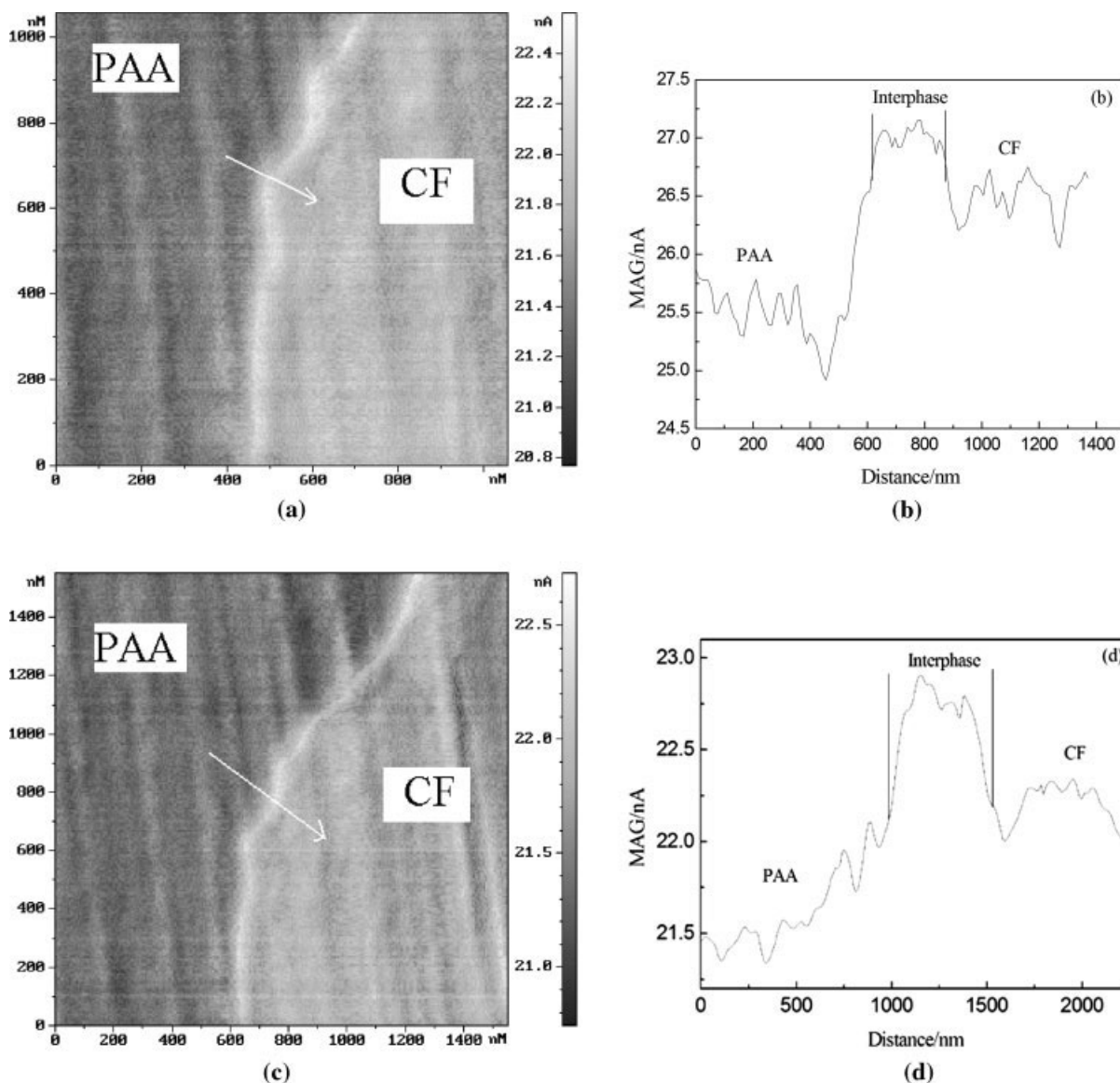


Figure 8 (a,c) Relative stiffness images and (b,d) line distributions of the relative stiffness of CF/PAA composites treated with (a,b) methacrylisobutyl-POSS and (c,d) trisilanophenyl-POSS.

that of the matrix but smaller than that of the CF. Thus, there was a transitional layer between the fiber and matrix. However, the interlayers between the CFs and PAA matrix formed by POSS coatings were hard or rigid according to the test of force-modulation-mode AFM, as shown in Figure 8. The relative stiffness was implicitly indicated by the detection of the magnitude (nA) of the flexural quantum of the microcantilever during the force-modulation-mode AFM test. The stiffness of the interface of the POSS-treated composites was larger not only than that of the PAA matrix but also than that of CFs, so there was no middle stiffness interlayer between the fiber and matrix. Thus, the increase in the impact properties may result from the cage nanostructure of POSS, but this is inconsistent with the conventional improve-

ment theory for fiber-matrix composites.^{22,23} The rigid interface resulted in the mismatch between the constituents in the CF/PAA composites. Experiments as well as models for brittle matrix composites have demonstrated that a strong interface is beneficial to the strength and toughness.²⁴⁻²⁶ By contrast, weak interfaces have been shown to be detrimental. Carère et al.²⁷ studied the influence of the interface on the crack deflection in brittle composites. Unfortunately, all the research concerned brittle ceramics, and there are natural differences between brittle PAA resins and brittle ceramics, although PAA is a very brittle resin that is made up of nonpolar, structural, ethynyl, aromatic hydrocarbons. Therefore, a new theory should be established to explain the mismatch of the modulus or stiffness in POSS-coating-treated

CF/PAA systems. Both IFSS and the initiation absorbed energy showed that the cube cage nanostructure of POSS was an important factor in improving the interfacial adhesion and impact properties at the same time. This could be explained as probably due to the nanoeffect of the POSS coating, which increased the resistance to deformation and the crack initiation of the resin.^{28,29} According to Figure 8, an interface with a certain thickness consists of a CF boundary layer, a POSS coating, and a PAA resin. If the content of POSS in the interfacial region is large enough that the interfacial region can be regarded as POSS-reinforced PAA resin nanocomposites, a hypothesis based on nanocomposites can help us to understand the improvement of the impact performance. In fact, it is reasonable that the interfacial region is considered to be nanocomposites on the basis of the micrographs of CF before and after the treatment. The mechanism of the toughness improvement of resin matrix composites with nanoparticles, such as CaCO_3 ^{30,31} or SiO_2 ,³² has been illuminated. When the composites are under load, the cracks in the matrix propagate to the fiber. The direction of the crack propagation is decided by the stress field of the crack tip and the mechanical properties of the interface and the fiber. If there is no appropriate interface, the stress field of the crack tip extends and generates a tensile stress, which is perpendicular to the crack in the intact fiber and leads to fiber fracture under lower stress. According to the hypothesis, the Si—O—Si cage nanostructure of POSS can induce more cracks to form while POSS-coating-treated composites are loaded. Thus, the initiation absorbed energy is increased after the treatment. After a crack is formed, the cage nanostructure of POSS can efficiently change the direction of the crack propagation, which increases the propagation absorbed energy. The stress around the POSS nanoparticles, the inducement of cracking, and the crack propagation orientation deflection by POSS nanoparticles are helpful for improving the impact properties of composites. In other words, the POSS cage nanostructure is the key factor when POSS is used as a coating on a fiber surface to improve the interface and impact properties of composites.

The results showed that the main contribution of the POSS coating was to improve the initiation energy during the impact event. This could be an indirect indication (corroborating the ILSS results and SEM images) that a better interface was present. Therefore, the stress transfer from the matrix to the fibers was more efficient. The mismatch of properties finally induced cracking at the interface, deflecting the main propagating crack and contributing to the increase in the final impact energy through the propagation term.

CONCLUSIONS

The effects of POSS-coating treatments of the surface on the interfacial and impact properties of CF-reinforced PAA matrix composites were studied with several characterization techniques. ILSS and IFSS of the CF/PAA composites were increased to different degrees after the fiber was treated with different POSS coatings. The increasing amounts of ILSS and IFSS of the CF/PAA composites after CF was treated with different POSS cage structural coatings were the same. Compared with those of the untreated composites, the initiation, propagation, and total absorbed energies of the CF/PAA composites treated with POSS coatings increased. SEM topographies of CF surfaces disclosed improved interactions between the fiber and PAA resin. The interface resulting from the POSS single-cage structural coatings was much harder than the PAA bulk resin and also somewhat harder than CFs according to the force-modulation-mode AFM test. Previous results indicated that there were improved interfaces caused by POSS coatings between the fiber and matrix and that they could increase the interfacial adhesion and the impact properties at the same time.

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