Siloxane Surfactant-Modified Clay and Its Effect in Reinforcing the Laminate of Polymethylsilsesquioxane

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ABSTRACT: To achieve good compatibility between clay layers and siloxane polymer, polymethylsilsesquioxane (PMSQ), montmorillonite was modified by a novel siloxane surfactant with $\bar{M}_w = 1900$ and then environmentally friendly solution-compounded with PMSQ to prepare glass fiber laminates. Transmission electronic microscope shows the orderly, exfoliated structure of the modified clay in PMSQ matrix; scanning electronic microscope demonstrates the fine dispersion of the clay layers in the matrix because of the good compatibility between the grafted surfactant and the matrix. Both the modified clay and its nanocomposite indicate much improved thermal stability. By incorporation of merely 0.3 wt % of the clay, the flexural modulus and strengths of fiber/PMSQ laminate are increased by 21 and 62%, respectively. This study illuminates the importance of the compatibility of the grafted siloxane surfactant with the matrix polymer in achieving both exfoliation and dispersion of clay as well as ideal mechanical properties for silicone-based polymers. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3974–3980, 2006

Key words: polymethylsilsesquioxane; clay; reinforcement; nanocomposites; laminate

INTRODUCTION

Polymer/clay nanocomposites are attracting a great deal of interest, from all around the world, as an effective way to overcome the shortcomings of conventional composites.[1,2] Depending on the arrangement of the silicate layers in polymer matrix, two types of morphology can be achieved: intercalated or exfoliated, of which the exfoliated structure has been recognized for a higher property improvement with lesser amount of clay. In general, three strategies, i.e., in situ intercalative polymerization, melt intercalation, and solution intercalation, were used to prepare nanoclay/polymer nanocomposites. The first method involves swelling the layered-silicate in the liquid monomer (or a monomer solution) to make the polymerization occur between the intercalated sheets. The process is complicated; however the exfoliation can be achieved by this approach. The melt intercalation is to mix the layered silicate with the polymer matrix in the molten state, which is suitable only for thermoplastic. For the third method, both clay and polymer are dispersed or dissolved in a solvent followed by evaporation of the solvent. As most of the involved solvents are toxic, its application is limited. If the chosen solvent is environmentally friendly, this efficient method to achieve exfoliation can find useful applications.

Polymethylsilsesquioxane (PMSQ) is a kind of organosilicon polymer with the empirical formula $(CH_3SiO_{3/2})_n$. Although it shows distinguished properties, such as high thermal stability, low dielectric constant, and UV resistance, PMSQ is brittle and sensitive to crack; its application has thus been limited. For instance, fiber/PMSQ laminate shows excellent thermal stability, but has poor interlaminar shear strength. Montmorillonite (MMT) has a layered structure, and is commonly used in preparing nanoclay/polymer nanocomposites. For each inorganic layer, the thickness is only 1 nm and the lateral size is about several hundreds of nanometers. Since each of the well-dispersed nanolayer can efficiently carry and transfer load the matrix PMSQ should be significantly reinforced by the addition of clay. Although a lot of studies show the improvement in mechanical property for orderly exfoliated epoxy/clay nanocomposite,[3–5] there are few reports on PMSQ reinforced by clay until now. Previously, we prepared PMSQ/clay nanocomposite by in situ intercalative polymerization.[6] Clay was organically modified by hexadecyltrimethylammonium bromide, and then swollen by a mixture of methanol and chloroform to facilitate the intercalation of monomer into the intergallery of the modified clay. Nevertheless, this method is a little

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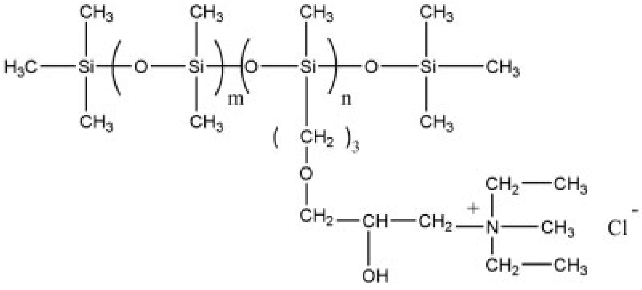

Figure 1 Structure of the siloxane surfactant D2.

complicated and it involves hazard solvent and achieves only intercalated structure.

In this study, clay is modified by a novel siloxane surfactant and then compounded with PMSQ by solution intercalation. Glass fiber is impregnated in the PMSQ/clay suspension to prepare glass fiber laminates. Considering application as well as environmental issues, we chose ethanol as the solvent. The X-ray diffraction (XRD) and transmission electron microscope (TEM) characterization show that clay is orderly exfoliated in the PMSQ matrix. The modulus and the flexural strength of the PMSQ laminate were significantly improved only with 0.3 wt % of clay.

EXPERIMENTAL

Materials

Siltech Corporation (Toronto, Canada) kindly provided the siloxane surfactant D2 ($\bar{M}_w$ = 1900), and the structure is shown in Figure 1. Sodium montmorillonite, with a cationic exchange capacity (CEC) of 120 mequiv/100 g, and clay-15A (Cloisite®15A) was obtained from by Southern Clay Products (Texas, USA). Woven glass fiber mat, with a thickness of 0.2 mm (EWR200–90), pretreated with a kind of silane coupling agent was supplied by Beijing FRC Research and Design Institute (Beijing, China).

Modification of clay by siloxane surfactant

One gram of clay was added to 1 kg of boiling distilled water, mixed, and heated for 5 min. A stoichiometric amount of the surfactant was dissolved in 100 g of water and then a given quantity of hydrochloric acid was added and stirred by a glass rod. The solution was slowly added to the clay suspension, and then the blend was vigorously stirred for 10 min at 80–90°C.

After modification, the clay suspension was rinsed with 5 kg of water. No Cl^- was detected by $AgNO_3$ after two times of rinsing. Then the suspension was washed four times additionally to thoroughly remove the ungrafted surfactants, and was condensed until slurry with concentration of 5 wt % of clay was obtained.

Preparation of PMSQ/clay–sil nanocomposites

The clay modified by the siloxane surfactant D2 (clay–sil) was dispersed in ethanol at a concentration of 0.2 g/100 mL, and sonicated for 30 min. The desired amount of PMSQ solution (34 g/100 mL ethanol) was added into the clay–sil suspension. Then the mixture was sonicated for another 30 min, magnetically stirred at room temperature for 60 min, and finally concentrated to 60 g/100 mL for the following laminate preparation. Samples for XRD were heated, dried, and milled finely.

Preparation of PMSQ/clay laminate

Concentrated PMSQ/clay–sil solution prepared using the aforementioned process was used to impregnate the glass fiber mat thoroughly, which is made up of bundles of fibers with diameter of 12 μm. The impregnated glass fiber mat was then exposed to air for 15 h to evaporate the solvent (ethanol). The dried impregnated mat was cut into pieces of desired size and stacked in a mold. When the mold was heated to 150°C at 15°C/min, 1 MPa of pressure was applied; the temperature was continued to increase until 175°C, and the mold kept at this temperature for 60 min. Finally, it was left to cool naturally at room temperature under pressed conditions.

Characterization

XRD characterization was performed on D/Max-2400 diffractometer using Cu kα (λ = 1.5418 Å) radiation (40 kV, 200 mA).

TEM observation was conducted on H9000NAR (HITACHI). The specimens were microtomed from the PMSQ/clay–sil nanocomposite with an ultramicrotome equipped with a diamond knife; sections were collected in a trough filled with water and placed on a 200 mesh copper grid.

The fracture surfaces of the laminate for scanning electronic microscope (SEM) observations were prepared by peeling off a ply from the laminate. The fracture surfaces were coated with platinum and observations were performed on HITACHI *S*-4300.

The flexural moduli and strengths of the obtained laminates were tested according to GB1449–83, which is similar to ASTM D-790.

Thermal gravimetric analysis (TGA) was performed on NETZSCH STA 409 PC/PG, with nitrogen flow rate of 30 mL/min, at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Modification of clay

As a comparison, a commercial organic clay, clay-15A, modified by dimethyldihydrogenatedtallow quaternary ammonium chloride, was used to prepare

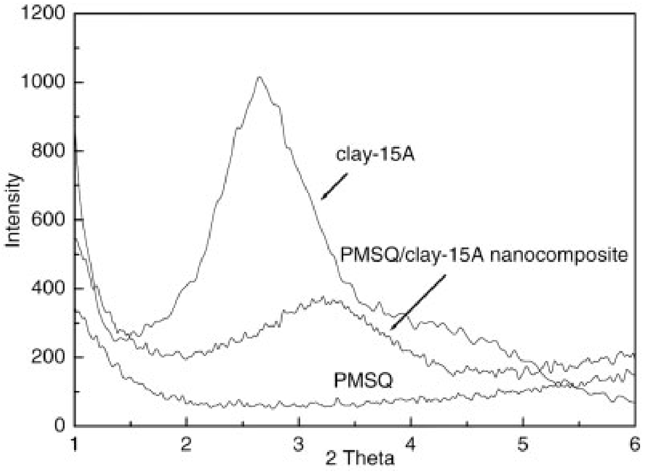

Figure 2 XRD patterns of PMSQ, clay-15A, and PMSQ/clay-15A containing 4.3 wt % of clay.

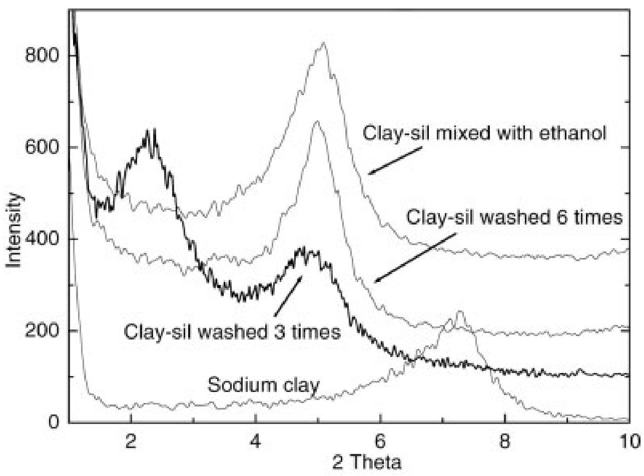

Figure 4 XRD patterns of sodium clay and clay–sil.

PMSQ/clay nanocomposite. In Figure 2, the XRD pattern of the clay shows a primary silicate (001) reflection at about 2.65°, corresponding to an interlayer spacing of around 3.33 nm. It was expected that the interlayer spacing of the organic clay should increase more or less after the polymer was solution-compounded. However, a broader but less intensive peak at around 3.3° was found for PMSQ/clay-15A nanocomposite, indicating a decreased interlayer spacing of 2.7 nm. There are two possible reasons for this unexpected result: the removal of the ungrafted surfactant, and the conformation change of the grafted surfactant. Since a certain amount of the surfactant used in the clay modification cannot often be grafted as desired, these ungrafted surfactant molecules often entangle with those grafted; hence, the ungrafted surfactant molecules are difficult to be removed completely unless heavily rinsed by a large amount of water. However, it is unnecessary to remove the ungrafted surfactant molecules as long as these molecules have nothing to do with the mechanical properties of the nanocomposites. Therefore, the reduction of the interlayer spacing of clay-15A after solution compounding, as shown in Figure 2, could be caused by the removal of the ungrafted surfactant molecules, since these molecules are dissolvable in the solvent ethanol. On the other hand, this reduction is also probably due to the conformation change of the surfactant molecules grafted on the surfaces of clay layers. Clay-15A was treated by dimethyldihydrogenated tallow quaternary ammonium chloride, which is a carbon-based molecule and is poorly compatible with any siloxane material. During the process of the solution-compounding, intercalation might be due to the solvent molecules instead of the PMSQ. Therefore, PMSQ plays no role in intercalation. This intercalated solvent can dissolve the surfactant molecules grafted on the surfaces of clay layers and may change their conformation from a disordered state to ordered state.

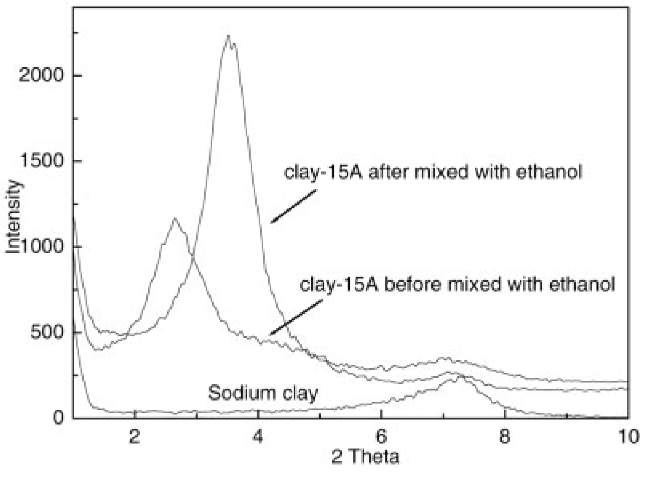

Figure 3 XRD patterns of sodium clay, clay-15A before and after mixing with ethanol.

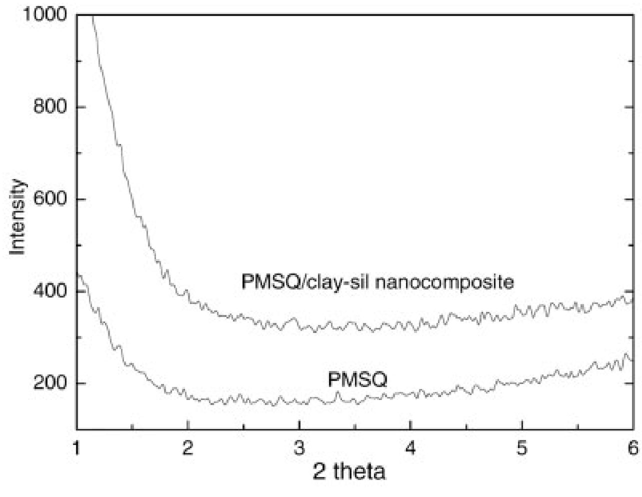

Figure 5 XRD patterns of PMSQ and PMSQ/clay–sil nanocomposite.

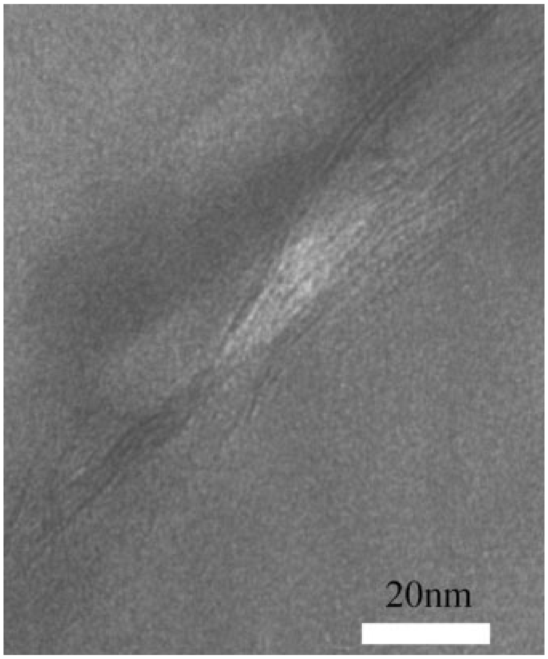

Figure 6 TEM image of PMSQ/clay–sil nanocomposite containing 2.8 wt % of clay.

The disordered conformation was formed during the preparation of clay-15A, in which sodium clay was dispersed in hot water and ion-exchanged with surfactant and finally precipitated in water after modification. Because water is not compatible with the grafted surfactant, the interlayer surfactant molecules adopt only a disordered conformation. In the present system, ethanol, a good solvent for the grafted surfactant, intercalates into the interlayer space so that the surfactant conformation can change from disorder to order. Since then, the ordered conformation has been kept during compounding as no water or other solvents were introduced into the system. Obviously, this ordered conformation shows smaller interlayer spacing than the disordered one.

To confirm the above analysis, an experiment was conducted, wherein clay-15A was dispersed in ethanol by a similar method to that of the preparation of the nanocomposites but without PMSQ. In Figure 3, a diffraction peak with an extraordinary intensity for the clay-15A, after mixing with ethanol, was found at 3.55°, corresponding to an interlayer spacing of 2.48 nm, while the clay-15A before mixing shows a pattern at 2.65°, indicating an interlayer spacing of 3.33 nm. The obviously decreased interlayer spacing after mixing implies that there is a removal of the ungrafted surfactant; the significantly increased diffraction intensity indicates the grafted surfactant conformation change in the interlayer space of clay-15A.

The result obtained in Figure 2 shows that the clay modified by carbon-based surfactant is not suitable for preparing PMSQ/clay nanocomposite. Therefore, we modified clay by a siloxane surfactant D2 with $\bar{M}_w = 1900$, such a high molecular weight ensured both exfoliation and good compatibility between the clay and the PMSQ matrix. This type of clay was previously mixed with a silicone rubber and exfoliation was achieved readily.[7] Hence, we prepared PMSQ/clay–sil nanocomposites in this work, hoping to achieve similar exfoliation. Figure 4 shows the influence of washing clay–sil with water and mixing clay–sil with ethanol, respectively, on the interlayer spacing of the clay–sil. After washing with water for three times, the clay–sil shows two diffraction peaks at 2.3° and 4.8°, respectively; and the clay–sil productivity is 62.5 wt %, since a certain amount of clay was lost during washing. However, the first peak at 2.3° disappeared after three more times of washing, which is caused by removal of the ungrafted surfactant molecules; and the productivity is further reduced to 31.2 wt %. For the clay–sil washed three times, the XRD peak intensity between 2.0 and 4.0 is higher in comparison with the intensity between 7.0 and 9.0; this indicates that there still exists an amount of ungrafted surfactant. Since an obviously reduced interlayer spacing of clay-15A was found after mixing with ethanol, the clay–sil was treated by a similar method so as to detect whether there are any ungrafted surfactant molecules

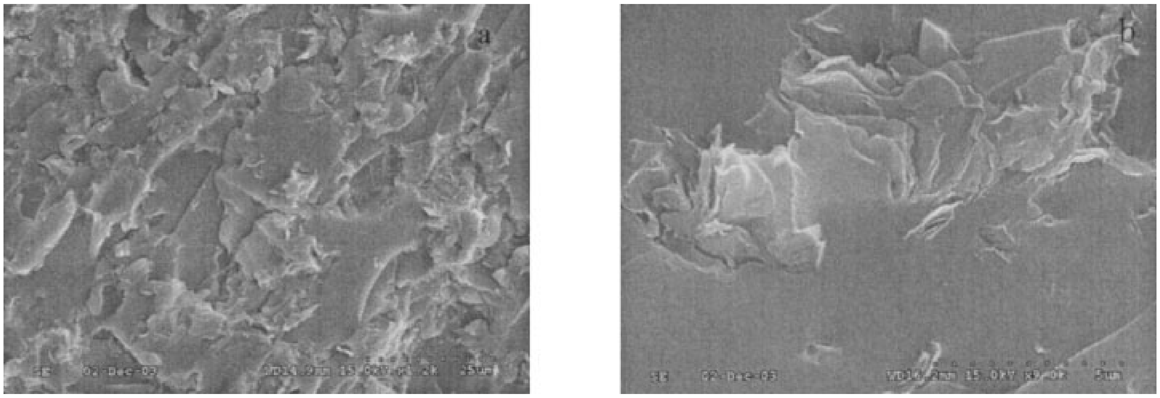

Figure 7 SEM images of PMSQ/clay-15A nanocomposite containing 4.3 wt % of clay: (a) at a lower magnification; (b) at a higher magnification.

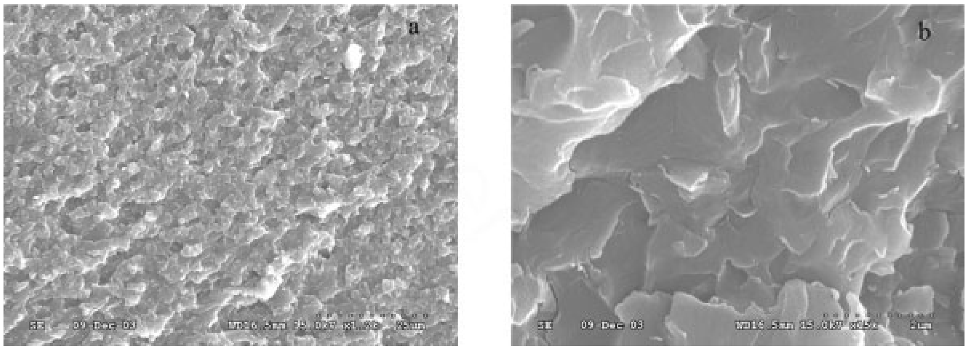

Figure 8 SEM images of PMSQ/clay–sil nanocomposite containing 2.8 wt % of clay: (a) at a lower magnification; (b) at a higher magnification.

in the interlayer space as well as a change in molecule conformation. In Figure 4, the XRD pattern of the clay–sil mixed with ethanol is quite similar to that of the clay–sil washed six times; indicating that nearly all the ungrafted surfactant molecules were removed by thoroughly washing, and no molecule conformation change occurred during mixing with ethanol.

After solution compounding with PMSQ, shown in Figure 5, no diffraction peak is visible, this shows clay–sil might be exfoliated.

Morphology of PMSQ/clay nanocomposites

The TEM photograph, shown in Figure 6, is a direct evidence for orderly exfoliated structure, in which layered structure is found, but the interlayer spacing is larger than 6 nm. This result is consistent with the featureless XRD of the PMSQ/clay–sil nanocomposite in Figure 5. Previous literature reported orderly exfoliated clay in epoxy resin, that is, no diffraction peak found in XRD but layered structure observed by TEM.[4,5,8,9] Therefore, it is concluded that clay–sil is orderly exfoliated in this research.SEM was employed to detect the dispersion of clay-15A and clay–sil in PMSQ. In Figure 7(a), clay-15A is not evenly dispersed and some aggregates or tactoids are found; Figure 7(b) shows the higher magnification image of the tactoid found in Figure 7(a). In comparison, the dispersion of clay–sil is much better in Figure 8(a) than that of clay-15A in Figure 7(a) at the same magnification; a similar conclusion can also be drawn from Figure 7(b) and Figure 8(b).

Thermal stability of PMSQ/clay–sil nanocomposite

As a nanofiller, inorganic clay is expected to increase the thermal stability of the polymer matrix. However, the carbon-based surfactants commonly used to modify sodium clay are less thermally stable; and this impedes the clay application because quite an amount of polymers are processed or/and used at above 200°C. As shown in Table I, the 5 wt % decomposition temperature of the clay–sil is about 45°C higher than that of clay-15A. This means clay–sil is of higher thermal stability than that of the clay modified by carbon-based surfactants.

TABLE I
Thermal Stabilities of Clay-15A and Clay–Sil by TGA

Sample	Clay-15A	Clay–sil
5 wt % decomposition temperature (°C)	260.7	306.1

In Figure 9, PMSQ/clay–sil nanocomposite containing 2.8 wt % clay indicates much improved thermal stability. The TGA result shows that 5 wt % decomposition temperature of the PMSQ/clay–sil nanocomposite reaches 516°C, 74°C higher than that of the pure PMSQ. The residues of the nanocomposite and the pure PMSQ at 700°C are 93.2 and 91.8%, respectively. Although the thermal stability of the clay–sil is superior to the clay modified with carbon-based surfactants, such as clay-15A, the weight loss of clay–sil is higher than that of PMSQ, as shown in Figure 9. And this means the inorganic part of the surfactant does not contribute to the improved thermal stability. Therefore, the thermal property improvement of PMSQ by incorporation of clay–sil can be attributed to

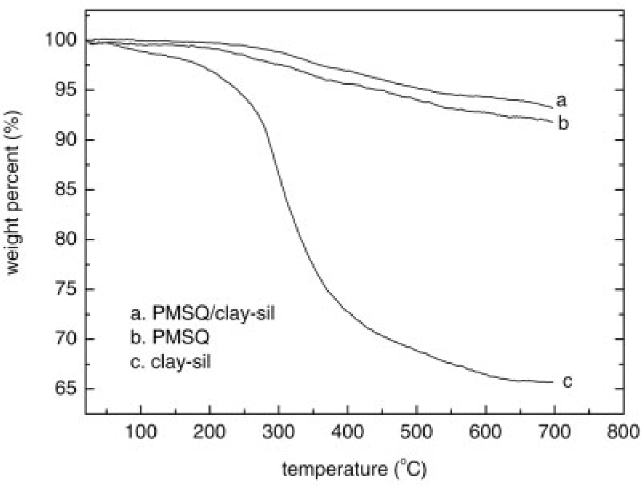

Figure 9 TGA characterization of clay–sil, PMSQ and PMSQ/clay–sil nanocomposite.

TABLE II
Flexural Modulus and Flexural Strength of Fiber/PMSQ/Clay–Sil Laminates

Number of laminate	Content of clay–sil (wt %)	Content of resin calculated (wt %)	Flexural modulus and its standard deviation (GPa)	Flexural strength and its standard deviation (MPa)
1	0	26.0	12.8 (1.4)	94.7 (14.5)
2	0.3	25.7	15.5 (0.4)	154.0 (12.7)
3	0.5	12.0	19.9 (1.1)	223.0 (25.7)
4	1.0	12.6	18.3 (1.0)	140.0 (21.9)

Five samples were tested for each data.

the shielding effect of the thermally stable clay layers embedded in the matrix, which reduces the permeability coefficient of volatile gases.[10]

Mechanical properties of glass fiber/PMSQ/clay–sil laminates

Although PMSQ has many attractive properties, it suffers from poor cohesive strength and hence poor mechanical strength. In load-bearing applications, glass fiber reinforced laminates are often used. The laminates made from such resins exhibit mechanical properties inferior to epoxy-type composites. One solution lies in the use of reinforcing fillers.[11]

The main obstacle for conventional fillers used in the fabrication of glass fiber laminates may come from the fact that they can not penetrate into the interfiber spaces together with the matrix and would be filtrated out. In our research, as a comparison, PMSQ solution containing 0.3 wt % clay-15A was first used to prepare glass fiber laminate. As a result, the obtained laminate showed a poor interlaminar strength such that the glass fiber sheets can hardly be bounded together. And this is due to the heavily aggregated state of the silicate layers in the matrix, which resembles conventional additives. The clay particles were filtered out and accumulated on the surface of the glass fiber mat, which prevented the matrix from adhering to the glass fiber surface, resulting in poor laminate strength.

Considering the matter of filler penetration, laminates with less than 1 wt % clay–sil content were prepared to investigate the effect of nanoclay filler on the mechanical properties of the laminates. As shown in Table II, both the flexural modulus and the flexural strength increase with addition of clay–sil. With 0.3 wt % addition of clay–sil, the flexural modulus and the flexural strength increase by 21 and 62%, respectively. This result shows that the clay–sil can effectively improve the mechanical performances of glass fiber/PMSQ laminates.

Explanation for this reinforcement of the laminate by clay–sil is as follows. Although the load-carrying ability of fiber composites with relatively weak polymer matrices is determined primarily by the fibers, the matrix plays a vital role in determining tensile strength, because of the fact that the strength of matrix-impregnated fiber bundles can be on the order of a factor-of-2 higher than the tensile strength of dry fiber bundles without matrix impregnation.[12] This can be understood by a synergistic effect between fiber and matrix. In a dry fiber bundle, when a fiber breaks down under load, it loses load-carrying ability over its entire length and this load has to be shifted to the remaining fibers. When most of the weaker fibers fail, the bundle fails. In a matrix-impregnated fiber bundle, however, the matrix bridges around individual fiber breaks so that the fiber can quickly pick up load-carrying ability from failed fibers. Thus, the adjacent fibers have to carry an increased load over only a small axial distance. Statistically, the distribution of fiber defects is likely even. Therefore, failure must occur at a higher load value after most of the fibers have failed in adjacent locations. The difference in

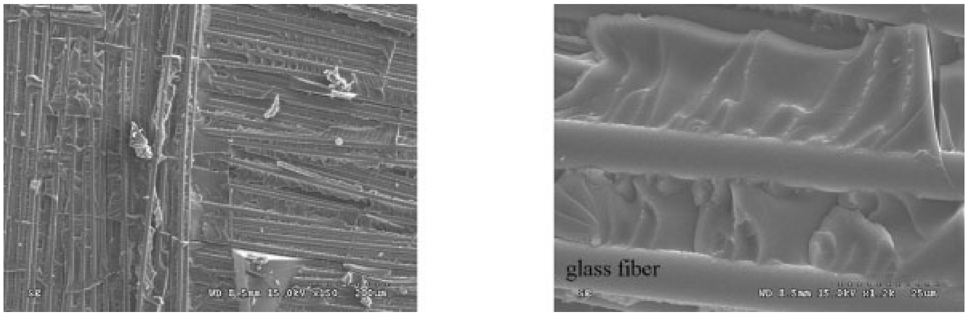

Figure 10 SEM images of fracture surface of glass fiber/PMSQ laminate. At a lower magnification (left); at a higher magnification (right).

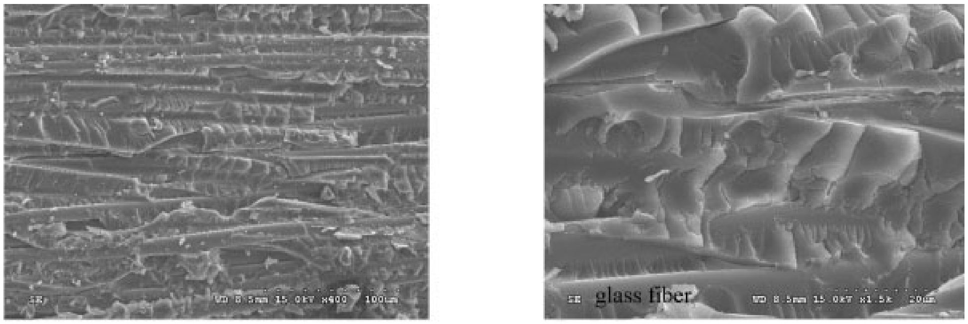

Figure 11 SEM images of fracture surface of fiber/PMSQ/clay–sil laminate containing 0.5 wt % of clay in PMSQ. At a lower magnification (left); at a higher magnification (right).

delivered fiber strength, determined primarily by the matrix strength and interface between fiber and the matrix, is a vital factor deciding the mechanical properties of laminates. In this study, both the flexural strength and modulus of the laminates increase significantly with addition of clay and this means a higher load-carrying ability of the matrix. As no further modification made on the fiber surface, this higher load-carrying ability must indicate higher matrix strength. The good compatibility between the siloxane polymer PMSQ and clay–sil made the clay exfoliated into thin nanoscale platelets in the matrix. Such thin platelets cannot be easily filtered out by glass fibers like clay-15A during the preparation. The good compatibility also generated strong interfacial strength between PMSQ matrix and the silicate platelets, enhancing the load delivery from matrix to the stiff silicate layers. As a result, the matrix was reinforced and the reinforced matrix is responsible for the enhanced property of the laminates.

Delamination, the separation of plies of laminates, is the most significant fracture mechanism for laminated composites compared to matrix cracking and durability. It often leads to significant loss of bending stiffness and strength. Hence, SEM was used in this research to study the delamination of fiber/PMSQ/clay–sil laminates. The fracture surfaces prepared by peeling off a ply from the corresponding laminates are shown in Figures 10 and 11. The fracture surfaces of the laminates with clay–sil are much coarser in Figure 11 than those without clay–sil in Figure 10. A coarser surface is thought to consume more energy whenever fracture occurs.[13] This explains the significant reinforcement of fiber/PMSQ laminate with addition of very small amount of clay–sil. Less effective reinforcing property for increased amount of clay–sil, for example, 1 wt % in Table II, might be the result of more interstices introduced into the matrix as the amount of clay platelets increased, as can also be seen in Figure 8.

CONCLUSIONS

Orderly exfoliated structure of clay in PMSQ/clay nanocomposite was obtained in this research by adopting a novel type of siloxane surfactant to modify clay. The thermal stability of the modified clay is higher than that of the commercial clay-15A; PMSQ/clay–sil nanocomposite also shows higher thermal stability than the pure PMSQ. Glass fiber/PMSQ laminates reinforced by 0.3 wt % of the clay–sil indicated significant improvement of the flexural moduli and flexural strengths. This is attributed to both clay exfoliation and its good compatibility with the polymer matrix. This research shows the important role of a siloxane surfactant in achieving ideal reinforcement for silicone/clay materials.

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