CHAPTER VII

ORGANOPHILIC BN THROUGH CATIONIC SURFACTANT ADSORPTION: ITS EFFECTS ON THE THERMAL CONDUCTIVITY AND MECHANICAL PROPERTIES OF BN-EPOXY COMPOSITE

7.1 Abstract

Various quaternary alkylammonium bromide surfactants were used to prepare the organophilic-BN filled epoxy composite. The interaction between alkylammonium bromide molecule and negative charge of boron nitride was investigated. The organophilic-BN particles were also prepared at different pHs of surfactant solution to investigate the correlation between the surfactant adsorption and pH of solution. Moreover, the decrease in specific surface area of modified BN was determined. The amount of adsorbed surfactant show that the surfactant adsorption depends on alkyl chain length and pH of the surfactant solution. The results also show that the surfactant adsorption led to an increase in the organophilicity of the BN surface and an enhancement in the interfacial adhesion between BN and the epoxy resin. These changes led to the improvement in thermal conductivity and mechanical properties of BN-filled epoxy composites.

Keywords: BN-filled epoxy composite; Cationic surfactant; Organophilic boron nitride; Thermal conductivity; Mechanical properties

7.2 Introduction

Recent advancement in electronics technology has resulted in the miniaturization of electronic devices, allowing more electronic devices to be integrated into a single device. Nevertheless, integration and cramming of electronic devices leads to the escalation of power dissipation as well as an increase in heat flux at the device. Therefore, it is essentially crucial for the heat generated from the device to be dissipated as quickly and effectively as possible, to maintain the operating temperatures of the device at a desired level [1, 2]. As the power density

becoming larger, the polymeric encapsulant is required to have a higher thermal conductivity to dissipate the huge heat and a low dielectric constant is required to avoid signal propagation delay.

Typically, the intrinsic thermal conductivity of polymers is very low as compared to other materials, for example, the thermal conductivity of epoxy, is only about 0.15-0.25 W/mK [3]. Since the inorganic ceramic has a high thermal conductivity, a thermally conductive composite can be manufactured by addition of ceramic fillers to the polymer. Epoxy composites have been widely used in both the power industry and the microelectronics industry because of their generally superior electrical, mechanical and thermal properties along with their economical and convenient processability. The properties of these epoxy/inorganic filler composites is controlled by the conductivity of inorganic filler and matrix, the interface conductance between filler and matrix, shape and size of the filler, and the concentration of filler [4]. However, most of inorganic ceramics are organophobic in nature leading to the poor wettability toward polymers and insufficient interfacial adhesion between filler and matrix due to the interfacial incompatibility between organic polymer and inorganic filler. It is known that the interfacial thermal contact resistance between different constituent phases in a composite can arise from the combination of a poor mechanical or chemical adherence at the interface and a thermal expansion mismatch. Thermal expansion mismatch may cause interfacial debonding in service due to different swelling/shrinkage characteristics [5]. Moreover, the heat transportation in inorganic ceramic is carried out by the flow of lattice vibration or phonons transportation, along the temperature gradient within the specimen. For a two phase system like polymer/filler composite, interfacial physical contact between polymer and filler is very critical, since phonons are very sensitive to surface defects [5].

Several researchers have studied the improvement in mechanical properties and interaction between silicate and polymer using alkylammonium ion [6-8]. In general, clay is hydrophilic in nature, which hinders the homogeneous dispersion in the organic polymer. Hence, clay should be swelled by alkylammonium material via cation exchange reaction between metal ion in clay gallery and alkyl ammonium ion in order for the polymer to penetrate into the clay gallery easily [6]. Dai *et al.* [7] found that, the organo-clay exhibited a better dispersion capability in epoxy resin matrix, reflecting a remarkable enhancement of physical properties. Moreover, Goloub [8] conducted a systematic study of the variation of surface charge with surfactant adsorption. They found that the greatest in surface charge is more pronounced with increase pH. The existing relatively high surface charge density reduces the surface hydrophobicity. This means that without careful pH control, pH changes may occur not only from isotherm to isotherm, but also along an isotherm. However, most studies reported only the initial pH [9].

Boron nitride (BN) has high thermal conductivity and excellent high temperature resistance, together with light weight and moderate cost, compared to other ceramic fillers [10]. The individual BN particle has a hexagonal platelet structure which consists of BN layers. Due to surface adsorption of moisture, the BN platelets can easily be in agglomeration form [10]. According to BN structure, the trapped air can occur at interparticle pores in agglomerated BN, that lead to the decreasing in thermal conductivity of BN.

In order to improve the thermal conductivity of epoxy composite, we will in this study investigate the thermal conductivity of organo-boron nitride (BN)-filled epoxy system. A series of alkylammonium bromide surfactants was used to understand the correlation between adsorption efficiency of BN and alkylammonium bromide with various chain lengths. The effect of surfactant adsorption on the thermal conductivity and mechanical properties was also investigated.

7.3 Experimental

7.3.1 Materials

The epoxy resin, bisphenol-A-(epichlorohydrin) (EPOTEC YD128), and the curing agent, cycloaliphaticamine (TH7301), were obtained from Aditya Birla Chemicals (Thailand) Ltd. The hexagonal BN (PCTL30MHF) with an average size of 30 micron was supplied by Saint-Gobain Ceramics and Plastics, Inc., USA. A series of cationic surfactants (C_nH_{2n+1})N(CH₃)₃Br with n = 12, 14, 16, and 18, were supplied from Fluka, Sigma-Aldrich, Inc., Singapore.

7.3.2 The Zeta Potential of BN Powders Measurement

The zeta potential of BN powder as a function of dispersion pH was measured with Zetazier 3000HSA, Malvern instrument. The BN powder was homogeneously dispersed in distilled water by sonication method. The pH of the aqueous BN suspension was adjusted using 0.1 M HCl and 0.1 M NaOH to cover the entire pH range under investigation (pH 2 to 10).

7.3.3 Preparation of Surfactant-Treated BN-Filled Epoxy Composites

To prepare the surfactant-treated BN, a 1.5 mM surfactant solution was added to BN powder by ratio of 1 g of BN to 10 mL of solution in 250 mL Erlenmeyer flask using rubber stopper and paraffin film to seal on top. This suspension was stirred at 80 °C for 5 h. the surfactant-treated BN particles were then filtered through a suction flask and washed with 100 mL deionized water to eliminate excess amount of surfactant. After filtration, the treated-BN particles were dried at 50°C for 24 h or until completely dried. In addition, the pH value of surfactant solutions was adjusted from 5.5, which is the initial value of deionized water to 6, 7, 8, 9, and 10, respectively, using 0.1 M NaOH before adding to BN powder to investigate the effect of pH on the absorption of surfactant on BN.

To prepare the composite, the surfactant-treated BN particles obtained above were first dried in a vacuum oven at 80 °C for 24 h prior to processing. The desired amount of dried BN was added into 60 mL of epoxy resin contained in a 250 mL plastic beaker. The loading of BN powder was 37 vol%. The mixture was then stirred by a mechanical stirrer (A.L.C. International S.r.l. Class I) at the mixing speed of 300 rpm for 30 mins. Next, 36 mL of curing agent was added into the mixture which was then stirred until homogeneous. The mixture was then poured into a stainless steel mold 70 x 90 x 3 mm³ in dimension. The open mold was then placed in a vacuum oven at 50 °C for 10 min to evacuate the entrapped air. The mold was then closed by a 26x26 cm² metal plate and placed in the compression molding machine under 15 tons of loading for curing at 80 °C for 1 h.

7.3.4 Determination of the Amount of Absorbed Surfactant on BN Particles

Organic carbon contents of the surfactant solutions before and after the adsorption were determined using a SHIMADZU TOC-VCSH organic carbon analyzer to obtain the TOC values of the solutions. The amount of absorbed surfactant on BN particles was then calculated from the TOC values by taking the difference in the TOC values before and after the adsorption.

7.3.5 Determination of the Specific Surface Area of Surfactant Treated-BN Particles

Nitrogen adsorption-desorption experiments were carried out on Quantachrome/Autosorb-1 Surface area analyzer. The specific surface area was calculated using the multi-point BET method which was repeated three times for each sample and the average value was reported.

7.3.6 Thermal Conductivity Measurement

Thermal conductivity of the composites was measured using a Hot Disk thermal analyzer (Hot Disk AB, Uppsala. Sweden). A minimum of three individual measurements were performed for each specimen (20 x 20x 3 mm³) with the sensor (3 mm diameter) being placed between two similar slabs of material. The sensor supplied a heat-pulse of 0.03 W for 15-20 s to the sample and the associated change in temperature was recorded. The average value of three specimens per sample was reported.

7.3.7 Determination of Flexural and Impact Properties

Flexural testing was performed based on ASTM D 790-98 using the three-point bending tests. The testing was conducted by using Instron series IX Automated Materials Testing System model 3366 with load cell of 10 kN. The crosshead displacement rate was set at 5 mm/min and the span length to thickness ratio was maintained at 16:1. The specimens used for flexural test were bars of 60 mm in length and 14 mm. in width. Three specimens were tested for each sample and the average value was reported.

Impact strength was determined using a Pendulum Impact Tester (Zwick, Germany) and the testing method was in accordance with ASTM D-256. For

each sample, five specimens measuring $63.5 \times 12.7 \times 3 \text{ mm}^3$ were tested and the average value was reported.

7.4 Results and Discussion

7.4.1 Effect of pH on the Zeta Potential of Aqueous BN Suspension

The behavior of particles in a solution is affected not only by mutual interaction of particles but also by interaction between the particles and the dispersion medium. When a particle is immersed in an aqueous solution, the adsorption of anions or cations leads to generation of a surface charge, and an electric potential develops between the surface and the dispersion medium. The charging of the surfaces of the particles is a basic property of the solid-solution interface in an aqueous environment. Figure 7.1 shows zeta potential of aqueous BN suspension as a function of pH in range of pH 2 to 10 without adding any supporting electrolyte to control the ionic strength. The zeta potential of BN powders had a small positive value at pH 2 and the point of zero charge (pzc) of BN powder was at pH 4.3. This result indicates that, down to about this pH, a negative net charge exists at the surface of BN and aqueous interface, which may result from preferential adsorption of negatively charged species on the BN surface and the surface charge becomes more negative with increase in pH. Necula et al [11] demonstrated that BN microparticles have a slight hydrophilic character and the surface charge of BN particles was dependent on the pH. This surface chemistry of BN is similar to mineral oxide [12]. According to this result, cationic surfactants were used to modify BN surface at pH value over 4.3 which is the suitable condition for the adsorption of cationic surfactants.

7.4.2 Effect of pH Value of Surfactant Solution and Alkyl Chain Length on Adsorbed Surfactant Content into BN Particles

The effect of pH value of surfactant solution on surfactant adsorption of BN particles is shown in Figure 7.2. The amount of adsorbed surfactant on BN surface increased with an increase in pH until it reached saturation at pH over 8. All the four surfactants showed the same trend. This result demonstrates that an increase in the amount of negative charge of BN surface led to an increase in the amount of adsorbed surfactant with the headgroups of cationic surfactant attaching to the negatively charged sites of BN surface. Zajac *et al.* [13] revealed that, when the surface charge density is relatively high, electrostatic interactions and hydrophobic effect are the principle driving forces of adsorption. Figure 7.3 shows the effect of alkyl chain length of surfactant on the amount of adsorbed surfactant on BN surface. The amount of surfactant adsorption increased slightly with increase in the alkyl chain length. The results show that the hydrophobic interactions between the tails of the surfactant molecules also played a part in surfactant adsorption. [14]. This hydrophobic interaction also brings about the more uniform hemi-micelle monolayer of long chain surfactant than that of short chain surfactant because the surfactant aggregation can occur at the solid surface as individual electrostatic adsorption of surfactant ions occurs [13, 15].

7.4.3 Effect of Alkyl Chain Length on the Water Contact Angle on BN Surface

The effect of alkyl chain length on the adsorption of surfactant molecules on BN surface was investigated by determining the contact angle of water droplet on BN surface treated with the four surfactants, as shown in Figure 7.4. The results show that the contact angle of water droplet on BN surface was higher than that of the original BN surface demonstrating that the hydrophobicity of BN surface was higher after the treatment. In addition, the contact angle of the shorter chain length of surfactant molecule is closer to the original BN than that of the longer chain surfactant because the hydrophilicity of shorter chain molecule is higher than that of the longer molecule.

7.4.4 Effect of Cationic Surfactant Adsorption on the Specific Surface Area of BN Particles

The specific surface areas and occupied surface area of original and modified BN particles at pH 8 were investigated and the results are shown in Table 1. The specific surface area (S_{BET}) of original BN particles was 7.46 m²/g which is close to values from others [16,17]. The results show that the adsorption of

surfactants could influence the surface area of the BN particles. However, the decrease in surface area of long alkyl chain molecule is greater than that of short chain molecule owing to the bigger size of the long alkyl chain surfactant [18]. Moreover, Table 1 also shows that the area occupied by surfactant molecule in A^2 /molecule also increased with an increase in alkyl chain length. Furthermore, Figure 7.5 shows the relationship between the amount of adsorbed surfactant and the occupied surface area on BN treated at pH 8. The results demonstrate that surfactants with longer alkyl chain length. This is to be expected as the surfactants with longer alkyl chain length. This is to be expected as the surfactants with longer alkyl chain length had higher adsorption and larger molecule than the ones with shorter chain.

7.4.5 Effect of Surfactant Adsorption on the Thermal Conductivity of Composite

The effect of the amount of adsorbed surfactant on thermal conductivity of composite was shown in Figure 7.6. The thermal conductivity of composite significantly increase from 1.9 W/mK for unmodified BN-filled composite to 3.4 W/mK for OTAB-modified BN-filled composite and linearly increased with increase in the amount of adsorbed surfactant for all the surfactants. This results show that surfactant-modified BN was more compatible with the epoxy resin leading to better contact between the two phases, and hence more efficient heat transfer was achieved.

Figure 7.7 shows that thermal conductivity of composite increased with an increase in the alkyl chain length at all pH. The results show that surfactants with longer alkyl chain length has better compatibility with the epoxy resin than those with shorter chain length.

7.4.6 Effect of Surfactant Adsorption on the Mechanical Properties of the Composite

7.4.6.1 Flexural Properties

To understand the influence of surfactant modification on the mechanical properties of the composite, the flexural strength and modulus of BNfilled epoxy composite were studied. The effects of the amount of HTAB surfactant adsorption at pH 8 on the flexural properties of the composite were shown in Figure 7.8(a). The result shows that both the flexural strength and modulus increased with increase in the amount of adsorbed surfactant due to the better wettability between BN and polymer matrix resulting from an improvement in organophilicity of BN through surfactant adsorption. Figure 7.8(b) shows the effect of alkyl chain length on the flexural properties of composite. The result shows that both the flexural strength and modulus increased with increase in the alkyl chain length. This was due to an increase in organophilicity of BN surface and the enhancement in polymer wettability resulting in the greater interaction between BN and polymer matrix. The greater interaction helped in effective force transfer over the interface between particle and matrix, and hence, better sharing of the acting forces leading to higher strength and modulus. Gopakumar et al [19] also found that the organophilic clay had increased modulus because of its greater interfacial adhesion with the polymer matrix. In addition, the correlation between thermal conductive property and flexural property was shown in Figure 7.8(c). With increase in thermal conductive property, both flexural strength and modulus increased indicating that surfactant modification not only assisted in the improvement in thermal conductivity of the composite, but also in enhancing their flexural properties.

7.4.6.2 Impact Property

The impact strength is an indication of the ability of the composite to withstand a sudden impact. Figure 7.9(a) shows the effect of adsorbed surfactant on impact strength. When the amount of adsorbed surfactant increased, the impact strength of composite slightly increased because of the increase in interfacial bonding between filler and matrix. Moreover, the effect of alkyl chain length on the impact strength of composite was investigated as shown in Figure 7.9(b). The result shows that the impact strength of BN filled composite increased with increase in alkyl chain length. This resulted from an improvement in organophilicity of BN and the better polymer penetration leading to an effective stress sharing among the particles, hence the higher impact strength. The correlation between impact property

and thermal conductive property was shown in Figure 7.9(c). While there was an increase in thermal conductive property, the impact strength also increased. This is due to the increase in orgranophilicity of BN particles through surfactant modification. Hence, both thermal and mechanical properties can be improved at the same time.

7.5 Conclusions

Our investigation showed that the cationic surfactant adsorption of BN particles increased linearly with increase in pH value up to pH 8 and also with increase in the alkyl chain length of the surfactant molecule. The increases in surfactant adsorption and the increase in surfactant chain length led to an increase in organophilicity of BN particle, and hence the thermal conductivity and mechanical properties of the BN-epoxy composite due to an improvement in the interfacial adhesion between the BN filler and the epoxy matrix.

7.6 References

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Surfactant	Molecular weight of surfactant	Surface area of surfactant-treated BN (m ² /g)	The occupied surface area of surfactant-treated BN (m ² /g)	The surface area occupied by surfactant (A ^{o2} /molecule)
DTAB	308.3	5.60	1.86	163.5
TTAB	336.4	4.80	2.66	222.0
НТАВ	364.5	3.70	3.76	300.3
OTAB	392.5	2.40	5.06	373.6

Table 7.1Surface area of BN particle and the area occupied by surfactant
molecule at pH 8.0.

Note: Surface area of original BN is 7.46 m^2/g



Figure 7.1 Zeta potential of boron nitride particles as a function of pH ($f(x) = 4.55+0.405x-0.466x^2+0.031x^3$).



Figure 7.2 The amount of adsorbed surfactant on BN surface as a function of pH value of surfactant solution (DTAB with $r^2 = 0.9486$, f(x)=0.67+0.15x, TTAB with $r^2=0.9780$, f(x)=0.87+0.14x, HTAB with $r^2=0.9851$, f(x)=1.03+0.13x, OTAB with $r^2=0.9964$, f(x)=1.30+0.12x).



Figure 7.3 The amount of adsorbed surfactant on BN particles as a function of chain length of surfactant at pH 5.5, 6.0, 7.0 and 8.0 (DTAB with $r^2 = 0.9869$, f(x)=0.53+0.078x, TTAB with $r^2=0.9788$, f(x)=0.78+0.068x, HTAB with $r^2=0.9767$, f(x)=1.07+0.058x, OTAB with $r^2=0.9849$, f(x)=1.09+0.064x).



Figure 7.4 Contact angle of water droplet on surfactant-treated BN surface.



Figure 7.5 The occupied surface area of surfactant-treated BN as a function of the amount of adsorbed surfactant (DTAB with $r^2=0.9352$, f(x)=1.34+0.94x, TTAB with $r^2=0.9261$, f(x)=1.79+1.20x, HTAB with $r^2=0.9999$, f(x)=1.87+1.70x, OTAB with $r^2=0.9405$, f(x)=1.11+2.13x).



Figure 7.6 Thermal conductivity of surfactant-treated BN-filled epoxy composite as a function of the amount of adsorbed surfactant at pH 5.5, 6.0, 7.0, and 8.0 (DTAB with $r^2=0.9500$, f(x)=1.01+0.89x, TTAB with $r^2=0.9784$, f(x)=0.92+1.00x, HTAB with $r^2=0.9841$, f(x)=0.84+1.09x, OTAB with $r^2=0.9945$, f(x)=0.74+1.18x).



Figure 7.7 Thermal conductivity of surfactant-treated BN-filled epoxy composite as a function of chain length of surfactant at pH 5.5, 6.0, 7.0, and 8.0.



Figure 7.8 (a) Flexural properties of HTAB-treated BN-filled epoxy composite at varying pH as a function of the amount of adsorbed surfactant.



Figure 7.8 (b) Flexural properties of surfactant-treated BN-filled epoxy composite as a function of chain length of surfactant at pH 8.



Figure 7.8 (c) Flexural properties of HTAB-treated BN-filled epoxy composite with varying pH as a function of thermal conductivity of HTAB-treated BN-filled composite.



Figure 7.9 (a) Impact properties of HTAB-treated BN-filled epoxy composite with varying pH as a function of the amount of adsorbed surfactant.



Figure 7.9 (b) Impact properties of surfactant-treated BN-filled epoxy composite as a function of chain length of surfactant at pH 8.



Figure 7.9 (c) Impact properties of HTAB-treated BN-filled epoxy composite with varying pH as a function of thermal conductivity of HTAB-treated BN-filled composite.