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Rheological and Thermomechanical Characterizations of Fumed Silica-filled Polybenzoxazine Nanocomposites

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Abstract. The composites of fumed silica-filled polybenzoxazine at various nanofiller contents ranging from 0 to 10 wt% were fabricated. In this study, the rheological and thermomechanical analysis of neat polybenzoxazine and its nanocomposites were performed. The rheograms show the shear thinning behaviours of the melted nanocomposite compound. In addition, the complex viscosity of the nanocomposites revealed that the liquefying temperature of these molding compounds increased with increasing the amount of fumed silica, while the gel-point temperature was not changed even though the amount of nanofiller was increased. The DSC thermograms confirmed that fumed silica loading had neither retarding nor accelerating effect on the thermal curing reaction of the benzoxazine monomer. Furthermore, the flexural modulus and microhardness of the nanocomposites were increased with an increase of the nanofiller. DMA thermograms also revealed that the glass transition temperatures (T_g) of neat polybenzoxazine were shifted from 157°C to higher values from the presence of the fumed silica.

1. Introduction

Polybenzoxazine is a newly developed class of thermosetting resins derived from ring-opening polymerization of their precursors. The polymer possesses various good properties such as high thermal stability, easy processability, low water absorption, near zero shrinkage after processing with excellent mechanical properties. The polymer can be synthesized using the patented solventless technology to yield a clean precursor without the need for solvent elimination or monomer purification [1]. Additionally; the polymer can be synthesized from inexpensive raw materials and does not release by-products during polymerization, thus showing high potential for various applications [2]-[4]. Although this novel polymer renders a lot of advantages, the shortcoming of common-type polybenzoxazine (PBA-a), polymer of 6,6'-(1-methylethylidene)-bis-(3,4-dihydro-3-phenyl-2H-1,3-benzoxazine, is its moderate glass transition temperature (ca 150°C) which limits the use in a harsh condition [5].

There are many researches reporting that compositing some thermosetting resins with inorganic nanofillers was able to improve the glass transition temperatures of the polymers, such as silica-vinyl ester [6], silica-epoxy [7]-[8], and silica-cyanate ester [9] nanocomposites to render higher glass transition temperature than neat polymers. Besides the glass transition temperature, inorganic nanoparticle-filled polymer composites have been classified as materials with the potential to significantly improve many properties over conventional microparticle-filled composites because the filler-matrix interface in these composites might constitute a much greater area and enhance the composite properties to a much greater extent at rather low filler concentration than microfillers [10]-[13]. Filler-filled nanocomposites exhibit outstanding improvement on properties which include the increase in modulus, strength, thermal stability, solvent resistance and the decrease of gas permeability and flammability [14]-[18].

Fumed silica, of which the specific surface areas typically range from 50 to 400 m^2/g, is one of the most commonly used nanofillers for many applications such as in electrical engineering, electronics and consumer goods [19]. The addition of this kind of nanofiller has a potential to improve heat distortion temperature, decrease moisture uptake, increase stiffness and strength, and increase flame resistance due to the size in nano scale and outstandingly high aspect ratio. Because of many beneficial points, the nanocomposites between the nanofiller and various polymers, such as epoxy [8]-[9], polypropylene [10], polyethylene [20], polyethylene terephthalate [21], cyanate ester [22]-[23] and silylated polyester [24], are the point of interest at present. However, there has been no investigation about fumed silica filled polybenzoxazine.

The objective of this study is to evaluate the effects of nanofiller contents on the thermal, rheological and thermo-mechanical properties of the polybenzoxazine/fumed silica nanocomposites. Furthermore, the effects on some mechanical properties such as flexural modulus, flexural strength and microhardness of the nanocomposites are also determined.

2. Experimental

2.1. Materials

The materials in this research were benzoxazine monomer and fumed silica. Benzoxazine monomer is based on bisphenol-A, aniline, and formaldehyde. Thai Polycarbonate Co., Ltd. (TPCC) supplied bisphenol-A (commercial grade). Paraformaldehyde (AR grade) was purchased from Merck Company and aniline (AR grade) was obtained from Panreac Quimica SA Company. Fumed silica (Reolosil$^®$ QS-20), from Tokuyama Co., Tokyo, Japan was kindly supplied by Cobra International Co., Ltd. All chemicals were used without further purification.

2.2. Benzoxazine Monomer Preparation

Benzoxazine monomer (BA-a) was synthesized from bisphenol-A, aniline, and paraformaldehyde at a 1:2:4 molar ratio. The mixture was stirred at 110 ^{o}C using the patented solventless technology [1],[25]. Normally, the monomer is solid powder at room temperature with yellow color. The powder was ground into fine powder and was kept in a refrigerator for further use without purification [2],[25],[26].

2.3. Fumed Silica Characteristics

The used fumed silica (nano-SiO_2) was Reolosil$^®$ QS-20 with the density of 2.2 g/cm^3. It is fluffy, white powder of amorphous structure. The average diameter of the spherical primary particles was varied from 5 to 50 nm, with nominal surface area of approximately 200 m^2/g.

2.4. Fumed Silica-filled Polybenzoxazine Nanocomposites Preparation

The samples were prepared with filler loadings of 0, 1, 3, 5, 7, and 10% by weight to yield molding compound. The fumed silica was firstly dried at 110 ^{o}C for 24 hours in an air-circulated oven until a constant weight was achieved and then kept in a desiccator at room temperature. Fumed silica was thoroughly mixed by hand with benzoxazine monomer in an aluminium container at about 120 ^{o}C and mechanically stirred to achieve good dispersion. Then, the compound was compression-molded by a hydraulic hot-press machine, in which the heating condition at 25 MPa was 160 ^{o}C for 2 hr and 180 ^{o}C for 2 hr. The thickness was controlled by using a metal spacer. After that, the specimens were post cured in an air-circulated oven at 200 ^{o}C for 4 hr. All samples were air-cooled to room temperature in the open mold before testing. The density of rendered composites was approximately 1.30 g/cm^3.

2.5. Characterization Methods

2.5.1. Differential Scanning Calorimetry (DSC)

Curing temperatures of fumed silica-filled polybenzoxazine composites were examined using a differential scanning calorimeter (DSC, model 2910) from TA Instruments. A 10 mg sample placed in a 50 μL aluminum pans was characterized at a heating rate of 10°C/min from 30°C to 300°C under nitrogen flux (50ml/min).

2.5.2. Rheological Measurements

Rheological properties of each alloy were examined using a Rheometer (Haake Rheo Stress 600, Thermo Electron Cooperation) equipped with parallel plate geometry. The measuring gap was set at 0.5 mm. The melt viscosity of the molding compound was performed under shear sweep mode at 120 ^{o}C, with the shear rate range of 5-300s^{-1}.

2.5.3. Thermogravimetric Analysis (TGA)

Thermal stability, degradation temperature (T$_d$) and char yield of fumed silica-filled polybenzoxazine composites were studied using a thermogravimetric analyzer (TG/DTA thermogravimetric analyzer model SII Diamond) from Perkin Elmer. The scans were performed from 30 to 900 ^{o}C at heating rate of 20 ^{o}C/min under oxygen flow (100 ml/min). The initial mass of a tested sample at around 20 mg was placed in a 70 μL ceramic cup with cover provided with venting holes. The degradation temperature at 5% weight loss and the char yield at 800 ^{o}C were recorded for each specimen.

2.5.4. Flexural Property Measurements

Flexural modulus and flexural strength of composite specimens were determined with a Universal Testing Machine (model 5567) from Instron Instrument with a 1 kN static load cell. The test method was a three-point bending mode with a support span of 32 mm and the crosshead speed of 1.2 mm/min. The dimension of the specimens was 50 mm x 25 mm x 2 mm. Five samples were used to determine the average property values.

2.5.5. Microhardness Testing

Microhardness of compressed specimens was measured utilizing a Vickers microhardness tester (model FM-700C) from Future-Tech. A pyramidal diamond was applied to the surface of the composite under a load of 4.90 N for 15 s. Diagonal length of the indentation was measured through a micrometric eyepiece with objective lens (50x magnifications). Each sample was measured repeatedly for ten times.

2.5.6. Dynamic Mechanical Analysis

Dynamic mechanical analyzer (DMA) model DMA242 from NETZSCH was used to investigate the dynamic mechanical properties of the specimens, i.e. storage modulus (G'), loss modulus (G''), loss tangent (tan δ) and glass transition temperature (T_g). The dimension of each specimen was 50 mm × 10 mm × 2 mm. The test was performed under bending mode. The strain was applied sinusoidally with a frequency of 1 Hz, and the specimen was heated at a rate of 5^oC/min from 30 to 270^oC. The glass transition temperature was reported as the maximum point on the loss modulus curve in the temperature sweep test.

2.5.7. Morphological Observation

The fractured surface of the composite specimen was observed with a JEOL JSM 6480LV scanning electron microscope at an acceleration voltage of 15 kV. All specimens were coated with a thin layer of gold using a JEOL ion sputtering device model JFC-1100E for 4 minutes to obtain a thickness of approximately 300 Angstroms.

3. Results and Discussion
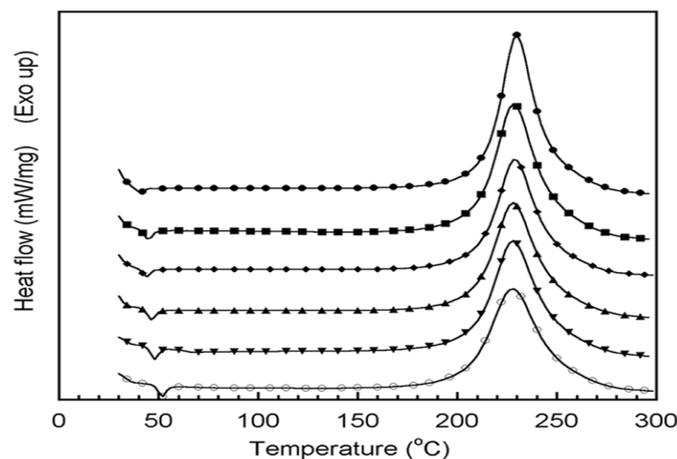
3.1. Curing Condition

Fig. 1. DSC thermograms of benzoxazine molding compound with various nanofiller contents:
(●) benzoxazine monomer, (■) 1wt%, (♦) 3wt%, (▲) 5wt%, (▼) 7wt%, (○) 10wt%.

Figure 1 shows the curing exotherms of neat benzoxazine monomer (BA-a) and the nanocomposites at different nano-SiO_2 contents. It reveals that the onset of curing was at 150^oC. The fumed silica filler is rather inert to the curing reaction. Furthermore, the area under the curing peak was found to decrease with increasing nano-SiO_2 content. That means the exothermic heat generated during curing decreases with decreasing the amount of benzoxazine monomer in the molding compounds.
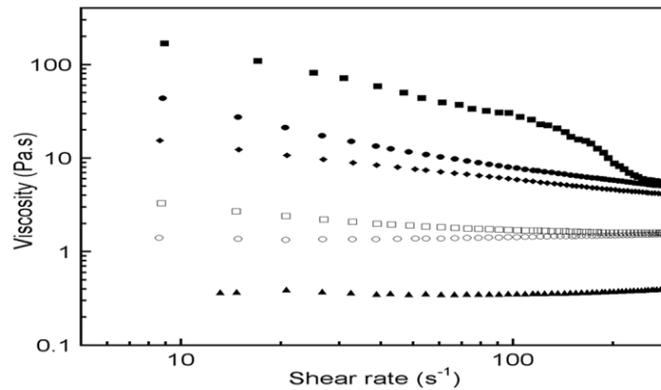
3.2. Rheological Behavior

Fig. 2. Viscosity of benzoxazine molding compound with different nano-SiO_2 contents at 120 °C: (▲) benzoxazine monomer, (○) 1wt%, (□) 3wt%, (♦) 5wt%, (●) 7wt%, (■) 10wt%.

The relation between apparent shear viscosity and apparent shear rate of nano-SiO_2 filled benzoxazine molding compound at various filler contents are shown in Fig. 2 in which the silica concentration were varied from 1 to 10 wt%, or expressed as volume fraction from 0.0054 to 0.0562. These volume fraction are based on the density of polybenzoxazine [28] (1.19 g/cm^3) and nano-SiO_2 [29] (2.22 g/cm^3) It can be seen that the shear viscosity of nano-SiO_2 filled benzoxazine molding compounds increases with increasing amount of nano-SiO_2. The results were as expected since nano-SiO_2 is common rheological filler used in many applications such as in the paint industry. In this study, the nano-SiO_2 filled benzoxazine molding compound exhibited shear thinning behaviors, which could be clearly observed at high nano-SiO_2 content, (i.e. 3 wt% or higher). Additionally, the viscosity of the compound at 10 wt% showed drastically decreased at the shear rate higher than 100 s^{-1}. These rheological behaviors were also found in the fumed silica suspensions in the bisphenol E cyanate ester [30], which reported that the mechanism of the decreasing viscosity with an increase in the shear rate should be attributed to a reduction in the effective volume of the aggregated silica particles caused by rearrangement of the particles without change in the size rather than by breaking them down under shear flow [30].
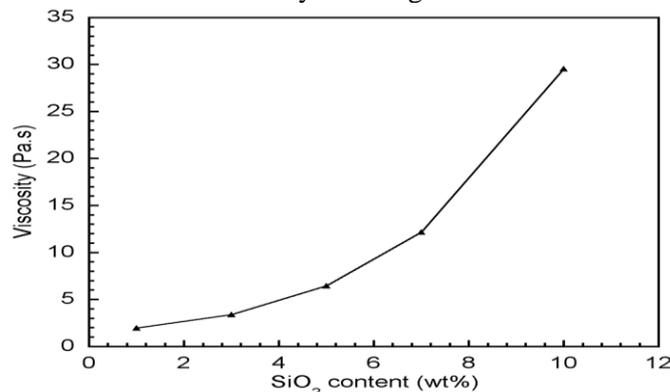

Fig. 3. Relation between nano-SiO_2 content and viscosity of benzoxazine molding compound

The relation between the shear viscosities of nano-SiO_2 filled benzoxazine molding compound and the filler contents was shown in Fig. 3. The results reveal that the shear viscosity increased with increasing nano-SiO_2 content, which is attributed to the fact that the colloidal forces between nanofiller particles can become enormous. The results show that even at low concentration, viscosity can be increase more than an order of magnitude. Theoretically, when the volume fraction is higher than 0.01, particles increasingly enter the neighborhood of other particles. Therefore the multiple particles interactions and particle-molten polymer interactions play an important role in the viscosity of the melted polymeric compound. In this study, the viscosity could be estimated from volume fraction via Batchelor Model [31].
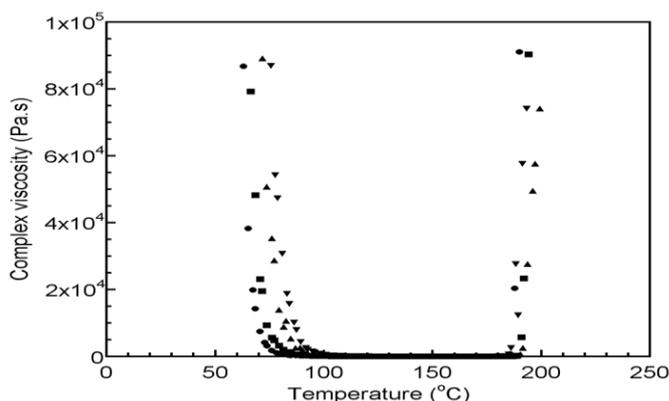
Fig. 4. Processing window of benzoxazine molding compound with different nano-SiO$_2$ contents: (●) 1wt%, (■) 3wt%, (♦) 5wt%, (▲) 7wt%, (▼) 10wt%.

Figure 4 reveals the processing windows of nano-SiO$_2$ filled benzoxazine molding compound. The complex viscosity of this molding compound at various nano-SiO$_2$ contents was recorded as a function of temperature. At the first stage, all the uncured molding compounds were solid at room temperature. They were changed to soft solid when temperature increased to reach their softening point. At this point, the dynamic viscosity of all nano-SiO$_2$ filled benzoxazine molding compound rapidly decreased. In the following stage, all molding compound became liquid, which possessed the lowest viscosity range. This period is informative because it is a processing window for a compounding process. In the final stage, at higher temperature all the nano-SiO$_2$ filled benzoxazine molding compound underwent the interaction past the gel point thus resulting in a rapid increase in the viscosity beyond this transition [32].

As can be seen from the rheograms in Fig. 4, the complex viscosities of the fumed silica-filled benzoxazine molding compound tended to increase with increasing the amount of nano-SiO$_2$. The liquefying temperature of these molding compounds also increased with increasing amount of nano-SiO$_2$. The lowest liquefying temperature of 70°C was showed for 1wt% of nano-SiO$_2$, while the highest liquefying temperature of 90°C was exhibited at the 10wt% of nano-SiO$_2$. In addition, the gel point of all molding compound was found to be constant at a temperature of 180°C, even though the amount of nano-SiO$_2$ was increased. Therefore, it can be concluded that nano-SiO$_2$ had no effect on the gel point temperature.

3.3. Thermogravimetric Analysis

The relation between nano-SiO$_2$ contents and char yield of nano-SiO$_2$ filled polybenzoxazine nanocomposites is depicted in Figure 5. From the plot, the amount of residual weight at 800 °C of the nano-SiO$_2$ filled polybenzoxazine composites was close to the actual amount of added nano-SiO$_2$ in composite. That is because the nano-filler, which has high thermal stability, starts to decompose at approximately more than 2000°C [29]. Thus nano-SiO$_2$ filler do not experience weight loss in the temperatures of 30-900°C. When the temperature increased to 800°C, only the component of polybenzoxazine was almost decomposed. Therefore, the amounts of char in this case are able to correspond to the amount of nano-SiO$_2$ presented in the composites. The inset of Fig. 5 depicts the 5wt% loss degradation temperature of the nanocomposites as a function of nano-SiO$_2$ contents. It could be seen that the degradation temperature of polybenzoxazine were found to significantly increase with the increase of nano-SiO$_2$. The 5wt% loss decomposition temperatures were in the range of 352-360°C comparing with that of 348°C of pure polybenzoxazine. The improvement of thermal stability was also found in similar systems between fumed silica and epoxy [33]. This phenomenon was attributed to the barrier effect of the inert nano-SiO$_2$ filler.
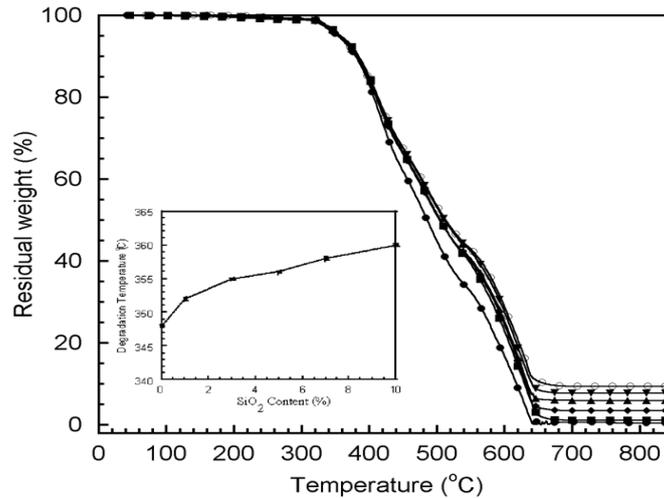
Fig. 5. TGA thermograms of the nanocomposites with different nano-SiO$_2$ contents:
(●) neat polybenzoxazine, (■) 1wt%, (♦) 3wt%, (▲) 5wt%, (▼) 7wt%, (○) 10wt%.
Inset of Fig. 5. Degradation temperature at 5% weight loss of nano-SiO$_2$ filled polybenzoxazine with various nano-SiO$_2$ contents.
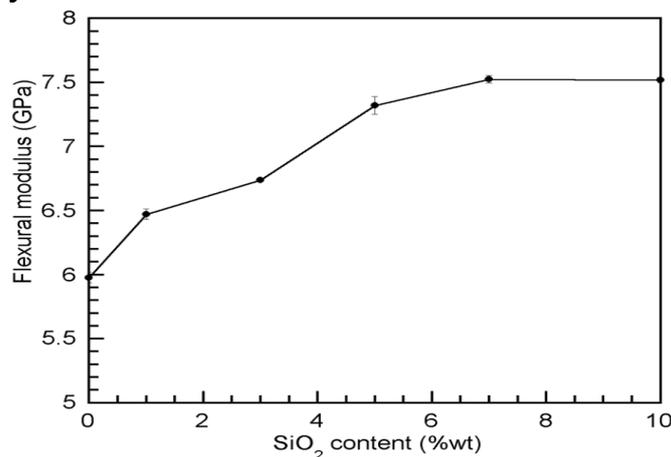
3.4. Flexural Property Measurement

Fig. 6. Relation between nano-SiO$_2$ content and flexural modulus of nanocomposites.
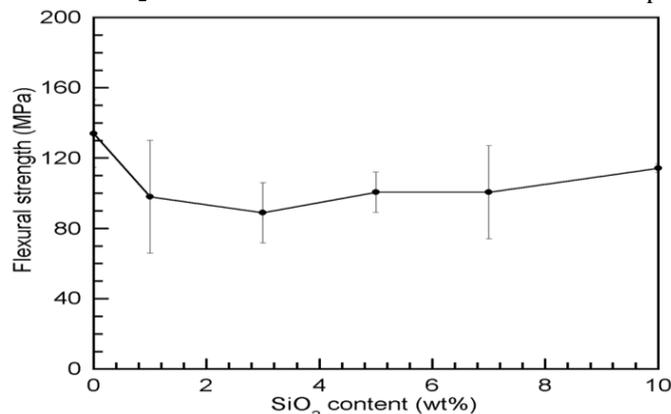

Fig. 7. Relation between nano-SiO$_2$ content and flexural strength of nanocomposites.

Flexural modulus and flexural strength of neat polybenzoxazine and fumed silica filled polybenzoxazine nanocomposite are illustrated as a function of nano-SiO$_2$ contents in Fig. 6 and 7, respectively. As shown in Fig. 6, the moduli of the nanocomposites were found to be substantially improved by the presence of nano-SiO$_2$. The flexural modulus of the neat polybenzoxazine was determined to be 5.98 GPa. When the nano-SiO$_2$ was applied, the moduli of the nanocomposites were

increased in the range from 6.47 GPa (or 10% increase at 1wt% nano-SiO$_2$) to 7.52 GPa (or 26% increase at 10wt% nano-SiO$_2$). The increase in modulus could be attributed to the reinforcing effect, i.e. the addition of rigid particulate filler into the polymer matrix was able to improve the stiffness of the polymer composite. Additionally, the increase of flexural modulus followed the rule of mixture. This phenomenon was similar to the mechanical properties of in the epoxy system was filled with nano-SiO$_2$ [34]-[35], Al$_2$O$_3$ and TiO$_2$ [36].

Figure 7 shows the flexural strength of the nanocomposites at various nano-SiO$_2$ contents, the results reveal that the nanocomposites render slightly lower flexural strength than the neat polybenzoxazine. Furthermore, the flexural strength of the filled polybenzoxazine was found to be relatively unchanged even though the filler contents were increased. It was postulated that the aggregation and agglomeration may present in the nano-SiO$_2$, which cause void defects in the composites. Thus the flexural strength values were slightly lowered. These observed phenomena were also found in the epoxy-silica nanoparticle system [35].
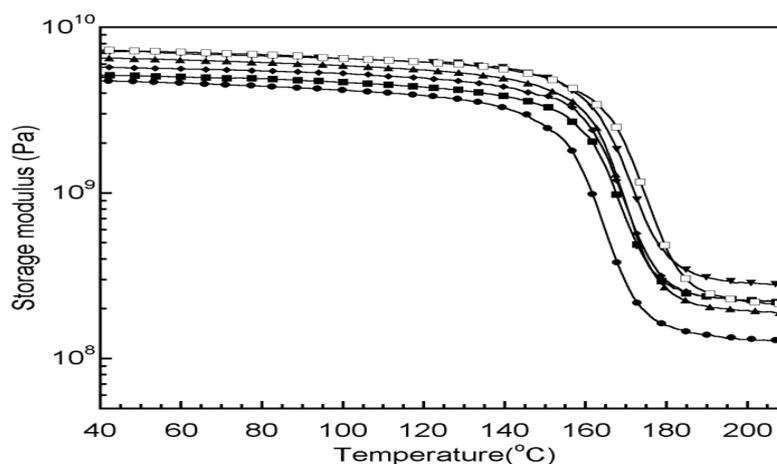
3.5. Dynamics Mechanical Measurement

Fig. 8. DMA thermograms of storage modulus with various nano-SiO$_2$ contents:
(●) neat polybenzoxazine, (■)1wt%, (♦) 3wt%, (▲) 5wt%, (▼) 7 wt%, (○) 10wt%.

Figures 8 and 9 illustrate the dynamic mechanical properties of their fumed silica-filled polybenzoxazine nanocomposites with various nano-SiO$_2$ contents. As seen in Fig. 8, at room temperature the storage moduli (G') of the nanocomposites increased with increasing nano-SiO$_2$ content. That is possibly due to the more rigid characteristics of nanofiller. Additionally, the storage modulus of neat polybenzoxazine (4.8GPa) was enhanced as the presence of fumed silica in the range of 5.2 GPa (at 1wt% nano-SiO$_2$) to 7.4 GPa (at 10wt% nano-SiO$_2$). It could be noticed that even only a small amount of nano-SiO$_2$ content in the composite was added, the dynamic mechanical properties was highly increased. The increase of storage modulus was also observed in the system of fumed silica-filled cyanate ester nanocomposite [23],[37] Moreover, the storage moduli values at high representative for the rubbery state increased remarkably as a result of the addition of nano-SiO$_2$. The influence is possibly attributed to the load transfer in the nanocomposite which occurs mainly through the filler nanoparticles. The results also indicate that the reinforcing effect of the nanofiller was in both glassy and rubbery states, which implied strong interfacial bonding between the polymer and the reinforcing nanofiller.

Figure 9 shows the loss moduli (G") curves of fumed silica-filled polybenzoxazine as a function of temperature. The maximum peak temperature in the loss moduli curve was indicated as a glass transition temperature (T$_g$) of the specimen as seen in the inset of this figure. The T$_g$ of neat polybenzoxazine (157°C) was increased with increasing the amount of nanofiller. The T$_g$ of the nanocomposite at 10wt% fumed silica was up to 167°C. The results from DMA measurement correspond to those from DSC thermograms. The increase of T$_g$ is possibly due to the presence of the silica that made the composite stiffer.
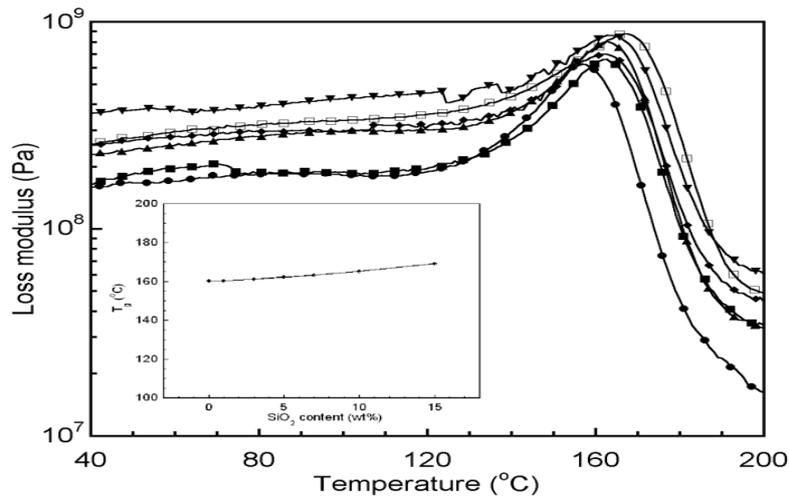
Fig. 9. DMA thermograms of loss modulus with various nano-SiO$_2$ contents: (●) neat polybenzoxazine, (■) 1wt%, (♦) 3wt%, (▲) 5wt%, (▼) 7wt%, (○) 10wt%.
Inset of Fig.9. Glass transition temperature of nano-SiO$_2$ filled polybenzoxazine nanocomposites with various nano-SiO$_2$ contents.

3.6. Micro-hardness Evaluation

Surface hardness is generally investigated as one of the most important factors related to the wear resistance of materials. Figure 10 exhibits the Vickers microhardness (HV) values of the neat polybenzoxazine and nano-SiO$_2$ filled polybenzoxazine composite at different nano-SiO$_2$ contents. The surface hardness of the nano-SiO$_2$ composite expectedly increased with increasing nano-SiO$_2$ filler content. When the nano-SiO$_2$ was applied, the HV value of neat polybenzoxazine (368 MPa) was raised from 375 MPa (at 1wt% nano-SiO$_2$) to 481 MPa (at 10wt% nano-SiO$_2$). Hence, the addition of nano-SiO$_2$ to polybenzoxazine was found to enhance the resistance of the polybenzoxazine deformation. This result was also found in the nano-SiO$_2$ filled epoxy composite system [35]. Moreover, the polybenzoxazine nanocomposite had greater increase in Vickers microhardness than that of the epoxy nanocomposite. Therefore, the wear resistant behaviors of the polybenzoxazine nanocomposites are under investigation into its potential use as a high wear resistant coating material.
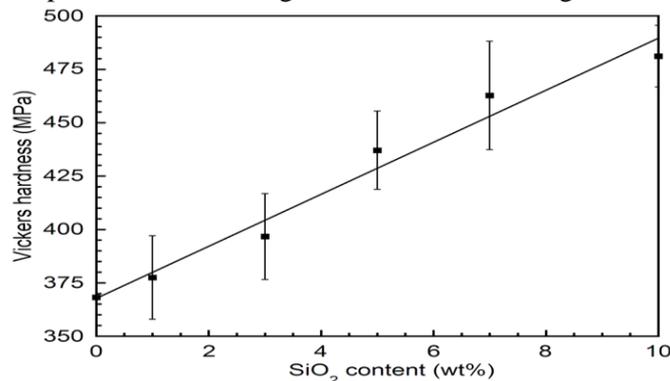

Fig. 10. Relation between nanofiller content and micro Vickers hardness of nano-SiO$_2$ filled polybenzoxazine.
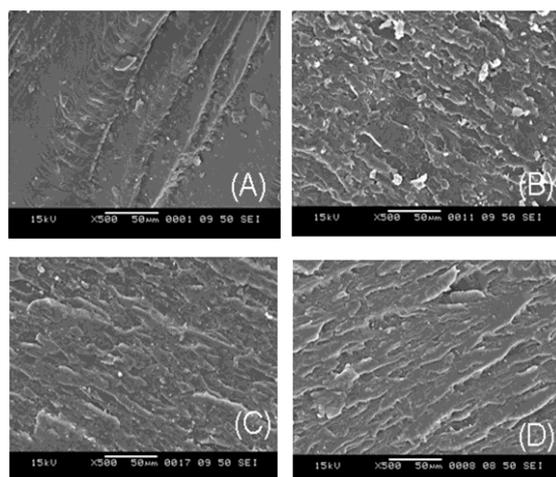
3.7. Morphological Observations

Fig. 11. SEM micrographs of fracture surface of the specimens with various nanofiller contents (x 500 magnification): (A) neat polybenzoxazine, (B) 3wt%, (C) 7wt%, (D) 10wt%.

Adhesion at the interface of inorganic fillers and polymers is one of the main factors determining the properties of polymer nanocomposites. The interfacial adhesion between phases has been examined by Scanning Electron Microscope (SEM). Figure 11 shows the fracture surface at 500x magnification of the fumed silica-filled polybenzoxazine nanocomposites. As seen in Fig. 11(a), the fracture surface of the neat polybenzoxazine is much smoother than that of the nanocomposites. However, the roughness on the fracture surface was increased with the addition of nano-SiO_2 as shown in Fig. 11(b) to (d). This suggested that the addition of fumed silica into polybenzoxazine matrix highly affects the fracture surface and brittle behavior of the composite matrix [38]. This phenomenon was similar to that occurred in the fumed silica- filled epoxy nanocomposite system [39].

4. Conclusions

The fumed silica-filled polybenzoxazine nanocomposites were prepared with filler contents varied from 1 wt% to 10wt%. DSC thermograms revealed that fumed silica loading had no significant effect on the thermal curing reaction of benzoxazine monomer. The rheograms of the melted nanocomposites compound showed the shear thinning behaviours. Furthermore, the complex viscosity of the nanocomposites suggested that the liquefying temperature of these molding compounds increased with increasing amount of nano-SiO_2, while the gel-point temperature was not changed even though the amount of nanofiller was increased. TGA thermograms revealed that the degradation temperatures of polybenzoxazine were significantly increased with an increase of the nano-SiO_2. The flexural modulus and micro hardness of the nanocomposites were also enhanced with an increase of the nanofiller.

5. Acknowledgements

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