

Thermal Stability and Thermo-Mechanical Properties of Nanoalumina-Filled Poly(benzoxazine-ester) Composite Films

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Nanoalumina-filled poly(benzoxazine ester) composite films were prepared by addition of various nanoalumina contents into poly(benzoxazine-ester) derived from bisphenol-A/3,5 dimethylaniline-based benzoxazine (BA-35x) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA). Chemical characteristics, thermomechanical properties, thermal stability, and thermal diffusivity of the composite films were investigated. The obtained results, i.e., degradation temperatures, glass transition temperatures, and thermal diffusivity properties of the composite films were enhanced with nanoalumina content. The composite film filled with 15 wt% of nanoalumina showed significant improvement in degradation temperature and solid residue, i.e., 404 °C and 62 %. The glass transition temperature of the composite film was increased with increasing nanoalumina content and exhibited a maximum value of 310 °C at 15 wt% of nanoalumina. IR spectra showed complete curing reaction and all characteristic peaks of the ester linkage and nanoalumina particles were observed in the poly(benzoxazine-ester) composite film. Based on the findings in this work, the poly(benzoxazine-ester) composite films can potentially be used in the case where a high stiffness and high thermal properties are required, i.e., coating film and polymeric matrix for fibre-reinforced composites.

1. Introduction

Thermosetting polymeric materials have been extensively used for the electronic, automotive, and aerospace industries in the form of composite matrices (Jubsilp et al., 2017), protecting coatings (Jubsilp et al., 2011), and microelectronic materials (Bachtrong et al., 2017), owing to their outstanding combination of thermal, mechanical, and electrical insulating properties. One of such thermosetting polymeric materials is composite materials, which are typically formed by combining two or more materials in such a way that the constituents of the composite materials are still distinguishable and not fully blended. These materials have attracted considerable attention as previous applications such as polymer composites filled with inorganic fillers, i.e., Al₂O₃, SiO₂, AlN, TiO₂, and BN, because inorganic materials exhibit excellent thermal stability and high dielectric properties, but high brittleness and bad film forming characteristics meanwhile polymers possess limitations for much higher performance applications in which inorganic materials are used. The composite production of polymers with inorganic materials has been suggested to meet the demands of balanced properties between polymers as organic materials and inorganic fillers, making them versatile in a wide range of applications.

In recent years, polybenzoxazine has been developed as a new class of thermosetting polymers based on the ring opening polymerization of benzoxazine precursors only by thermally cure without generating by-product of volatiles. The polymer combines good mechanical performance and molecular design flexibility of epoxy resins with high thermal properties and flame retardance of phenolic resins. The chemistry of benzoxazine synthesis offers a wide range of molecular design flexibility by using derivatives of phenol, formaldehyde, or primary amine. Moreover, polybenzoxazines possess several outstanding properties such as near-zero shrinkage after curing, low water absorption, and relatively high glass transition temperature (T_g) even though they render relatively low cross-linking density (Ishida and Agag, 2011). Because of the polybenzoxazine-based polymeric materials

applications have diversified, the improvement of the properties of new polymer products, particularly by modification of the existing polymers, continues to be essential. To achieve toughness, high thermal stability, high char yield, and high T_g for an advanced material system, blending of rigid polybenzoxazine with other resins or polymers provides the polybenzoxazine with even broader range of applications as a performance improvement of bisphenol-A-aniline type polybenzoxazine by blending with polyimide (PI) has been reported that T_g values and thermal stabilities of the blends increased as the PI component increased (Takeichi et al., 2005). In addition, fluorine-containing copolybenzoxazines were successfully prepared by reacting bisphenol-AF/aniline-based benzoxazine resin (BAF-a) with 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) (Pattharasirivong et al., 2017). It was found that the copolymers showed superior degradation temperature and significant improvement in char yield and the incorporation of fluorine groups into polybenzoxazine was found to substantially decrease the dielectric constant of the resulting copolybenzoxazine to as low as 2.6. The obtained copolymers are appropriate for applications as polymeric films for coatings and as a good electrical insulation material with high thermal resistance. Furthermore, the modification of a bisphenol-A/aniline based polybenzoxazine with aromatic carboxylic dianhydride, i.e., BTDA, BPDA, and PMDA have been investigated (Jubsilp et al., 2012). The obtained copolymer films exhibited excellent toughness, high thermal stability, and good mechanical properties. It is possible that the copolymers may be considered as potential candidates for high thermal and mechanical properties with fire resistant characteristics.

The main objective of this research is to develop composite films of nanoalumina-filled polybenzoxazine modified with 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA). The chemical, thermal, and mechanical characteristics of the composite films with different amounts of nanoalumina were discussed based on the results of Fourier transform infrared spectroscopy (FTIR), dynamic mechanical analyser (DMA), thermogravimetric analyser (TGA), and thermal wave analysis (TWA).

2. Experimental part

2.1 Materials

Materials used in this study are bifunctional benzoxazine resin (BA-35x) based on bisphenol-A (polycarbonate grade, Thai Polycarbonate Co., Ltd. (TPCC)), para-formaldehyde (Merck Co.) and 3,5-dimethylaniline (98 %, Fluka Chemical), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA, Sigma Aldrich Thailand Ltd.) and *N*-Methylpyrrolidone (NMP, Wako Pure Chemical Industries, Ltd.) as a solvent. The BA-35x was synthesized according to the patented solventless technology (Ishida, 1996). Nanoalumina particles, which have the average particle size of 13 nm were purchased from Sigma Aldrich Japan Ltd. and used as received.

2.2 Preparation of BA-35x:BTDA copolymers and their composites

Each resin component was first measured at the desirable mole ratios. The monomer mixture to be investigated was BA-35x:BTDA ranging from 1:0.25 to 1:1. The mixture was dissolved in NMP solvent and stirred at 80 °C until a homogeneous solution was obtained. Then, the obtained liquid mixture was cast on glass plate. The NMP solvent was then removed by drying the sample in a vacuum oven at 60 °C for 2 h before undergoing a step cure in a conventional oven. The sample was then cured sequentially at 170 °C for 1 h and at 190 °C, 210 °C and 230 °C for 2 h each to ensure a fully cure stage of the mixture.

Nanoalumina-filled poly(benzoxazine-ester) composite films were prepared by dispersing nanoalumina particles in NMP while vigorously being stirred under ultrasonication for 2 h. The BA-35x:BTDA (1:0.67) solution was then added into the suspension and stirred with a mechanical stirrer to yield a homogenous (BA-35x:BTDA)/nanoalumina suspension. Then, the obtained suspension was casted on treated glass plate. The NMP solvent was then removed by drying the sample in a vacuum oven at 60 °C for 2 h before undergoing a step cure in a conventional oven. The sample was then cured sequentially at 170 °C for 1 h and at 190 °C, 210 °C and 230 °C for 2 h each. The composite films were then allowed to cool to room temperature.

2.3 Sample characterizations

Infrared (IR) spectra were recorded using a JASCO (Hachioji, Japan) Fourier Transform IR-420 spectrophotometer equipped with an ATR 450-S unit. Far-infrared (Far-IR) spectra were measured with a JASCO FT-IR-6100 spectrometer in the range of 650 – 250 cm^{-1} .

Dynamic viscoelastic measurements of the films were conducted under tension mode on an Orientec Rheovibron DDV-01FP automatic dynamic viscoelastomer at 35 Hz at a heating rate of 4 °C/min. The film was heated from 25 °C to 400 °C. The glass transition temperature was taken from the temperature at the maximum point on the loss modulus curve.

The weight loss of a film as a function of temperature was monitored using a thermogravimetric analyser (TGA) from Rigaku Corporation (model Thermo Plus 2 TG-DTA TG8120). The weight of the film was measured to be

about 10.0 mg. The films were heated at a rate of 5 °C/min from 30 °C to 850 °C under argon atmosphere at 100 mL/min.

The thermal diffusivities at room temperature along the out-of-plane direction (D_{\perp}) of samples were measured with an AC temperature wave analyser (ai-Phase mobile 1, ai-Phase Co.Ltd.)

3. Results and discussion

3.1 Viscoelastic property, thermal stability, and network formation of BA-35x:BTDA copolymer films

A series of a novel poly(benzoxazine-ester) copolymer films based on bisphenol A/3,5-dimethylaniline (BA-35x) and BTDA at BA-35x:BTDA mole ratios of 1:0, 1:0.25, 1:0.33, 1:0.50, 1:0.67, and 1:1 were prepared. In Table 1, storage modulus in a glassy state of the copolymer films was found to increase with increasing BTDA mole ratio up to 0.67 and then decreased as the storage moduli of the copolymer films were enhanced from 3.57 GPa for BA-35x:BTDA (1:0.25) to 4.05 GPa for BA-35x:BTDA (1:0.67) which are higher than that of PMR-15 type polyimide (2.50 GPa) (Abdella et al., 2002) and s-BPDA/ODA type polyimide (3.00 GPa) (Rimdsut et al., 2007). Furthermore, glass transition temperatures (T_g s) of the copolymer films observed from loss modulus curve at the peak position are higher than that of the polybenzoxazine (poly(BA-35x)) and the values also increased with increasing BTDA contents up to 0.67 mole and then slightly decreased. Specifically, the poly(benzoxazine-ester) copolymer film prepared from a mole ratio of BA-35x:BTDA (1:0.67) exhibited the highest T_g of 300 °C that is substantially higher than that of the poly(BA-35x), i.e., 260 °C. In addition, the copolymer films exhibit thermal stability with thermal degradation temperature at 10 % weight loss (T_{d10}) and char yield at 800 °C ranging from 378 °C to 398 °C and from 54 % to 57 %, respectively, which significantly increased compared to those of the poly(BA-35x), i.e., T_{d10} = 362 °C and char yield at 800 °C of 49 %. The ester linkage formation between hydroxyl group of the polybenzoxazine and anhydride group of the BTDA confirmed by FTIR was expected for the enhanced thermal stabilities of these copolymer films as similarly observed in the previous publication (Jubsilp et al., 2011).

Table 1 Viscoelastic property and thermal stability of BA-35x:BTDA copolymer films

BA-35x:BTDA (mole ratio)	E' (GPa)	T_g from E'' (°C)	T_{d10} (°C)	Char yield at 800 °C (%)
Poly(BA-35x)	3.00	260	362	49
1:0.25	3.57	270	378	54
1:0.33	3.60	285	389	57
1:0.50	3.83	295	383	57
1:0.67	4.05	300	387	55
1:1	3.40	290	398	57
BTDA	-	-	317	2.5

Figure 1 shows IR spectra of BA-35x monomer, BTDA, poly(BA-35x), and poly(benzoxazine-ester) copolymer. BA-35x monomer was characterized by the band at 1,232 cm^{-1} from the aromatic ether C-O-C stretching mode of an oxazine ring whereas the band around 1,497 and 947 cm^{-1} were attributed to the tri-substituted benzene ring. After fully thermal cure, these bands completely disappeared indicating a complete loss of the oxazine ring in the BA-35x monomer. In addition, new absorption peaks of the tetra-substituted aromatic ring at 1,488 cm^{-1} and the asymmetric stretching of C-N-C in the regions 1,240 – 1,020 cm^{-1} were observed, suggesting the ring opening reaction to take place ortho to the phenolic moiety as displayed in poly(BA-35x) curve and the appearance of a broad peak about 3,300 cm^{-1} which assigned to the phenolic hydroxyl group after ring opening reaction of BA-35x monomer by thermal cure was also observed. For the BTDA, the IR spectrum revealed the anhydride adsorbed at 1,860 and 1,780 cm^{-1} . In addition, the band centred at 1,232 cm^{-1} associated with the C-O-C stretching mode in the BTDA was also detected. To confirm the formation of ester linkage in the poly(benzoxazine-ester) copolymer based on the mole ratio of BA-35x:BTDA (1:0.67), the characteristic absorption bands of the ester groups near 1,735 cm^{-1} (C=O stretch) and 1,100 cm^{-1} (C-O stretch) were observed in the FTIR spectra, while the characteristic absorption of the anhydride groups at 1,860 and 1,780 cm^{-1} did not appear in the spectra, indicating that the reaction formation is complete. Furthermore, the characteristic vibration bands of the copolymer were also observed at 3,670 – 3,100 cm^{-1} (O-H stretch in phenol and carboxylic acid), 1,370 cm^{-1} (isopropyl group) and 740 cm^{-1} (CH out-of-plane deformation in meta-disubstituted benzenes).

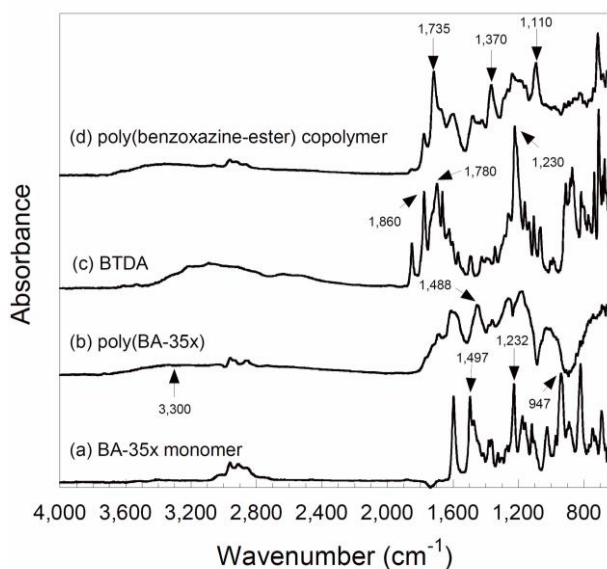


Figure 1: IR spectra: (a) BA-35x monomer, (b) BTDA, (c) poly(BA-35x), (d) poly(benzoxazine-ester) copolymer based on the mole ratio of BA-35x:BTDA (1:0.67)

3.2 Properties of nanoalumina-filled poly(benzoxazine-ester) composite films

From Table 1, it can be seen that the presence of BTDA into poly(BA-35x) to form poly(benzoxazine-ester) copolymers at mole ratio of BA-35x:BTDA (1:0.67) displayed good mechanical and relatively high glass transition temperature. Therefore, the BA-35x:BTDA (1:0.67)-based poly(benzoxazine-ester) copolymer filled with nanoalumina in a range of 0-20 wt% was prepared. Thermomechanical properties, i.e., storage modulus and glass transition temperature (T_g) observed from loss modulus curve at the peak position of the copolymer filled with nanoalumina in a range of 0-20 wt% were measured by DMA. It was found that the storage modulus at 25 °C tended to increase with increasing nanoalumina content, i.e., 3.75 GPa, 4.03 GPa, 4.11 GPa, and 3.71 GPa for 5, 10, 15, and 20 wt% nanoalumina, respectively, whereas that of the poly(benzoxazine-ester) copolymer was measured to be 4.05 GPa. However, an initial decrease in the storage modulus from 4.05 GPa to 3.75 GPa was observed when 5 wt% nanoalumina is added in the copolymer. This behaviour may be due to toughening effect formation. The T_g s of the composite films are higher than that of the poly(benzoxazine-ester) copolymer and the values increased with increasing nanoalumina content as the T_g of the copolymer was 300 °C, while the addition of nanoalumina at 5, 10, and 15 wt% shifted the T_g to 302 °C, 305 °C, and 310 °C, respectively. The T_g improvement of the composite films may be due to the molecular interactions in the interfacial region between the nanoalumina particle surface and the polymer medium. The oxygen plays a dual role by involving in covalent bonding with the polymer chain and electrostatic bonding interactions with the nanoalumina particles (Alias et al., 2011). Conversely, the decrease in the T_g of the composite film filled with 20 wt% nanoalumina, i.e., 280 °C was observed. This suggests that poor dispersion was attained in high content due to the agglomeration of the nanoalumina particles.

TGA curves of the poly(benzoxazine-ester) copolymer and its composite films are depicted in Figure 2a. It was found that the addition of 5-20 wt% nanoalumina into poly(benzoxazine-ester) copolymer film based on BA-35x:BTDA (1:0.67) have improved thermal stability. The T_{d10} of the composite films was 397 °C, 407 °C, 404 °C, and 394 °C, solid residue at 800 °C was 59 %, 60 %, 62 %, and 64 % for 5, 10, 15, and 20 wt% nanoalumina, which significantly increased compared to those of the poly(benzoxazine-ester) copolymer film, i.e., T_{d10} = 387 °C and solid residue at 800 °C of 55 %. It might be due to the presence of nanoalumina which restrains the movement of poly(benzoxazine-ester) copolymer main chain and limits the segmental movements in the copolymer matrix and hence reduces the degradation rate. More energy is consumed to initiate and continue the chain movement in the copolymer, higher degradation temperatures are required. In addition, this characteristic suggested good dispersal state of nanoalumina particles in the copolymer matrix and there was also significant interaction between the nanoalumina particles and the copolymer as it can be confirmed being a nanoalumina particle in the copolymer matrix by Far-Infrared (Far-IR). The IR curve of the nanoalumina-filled poly(benzoxazine-ester) composite exhibited an absorption band in the range of 640 – 600 cm^{-1} while that of the poly(benzoxazine-ester) copolymer disappeared as can be seen in Figure 2b.

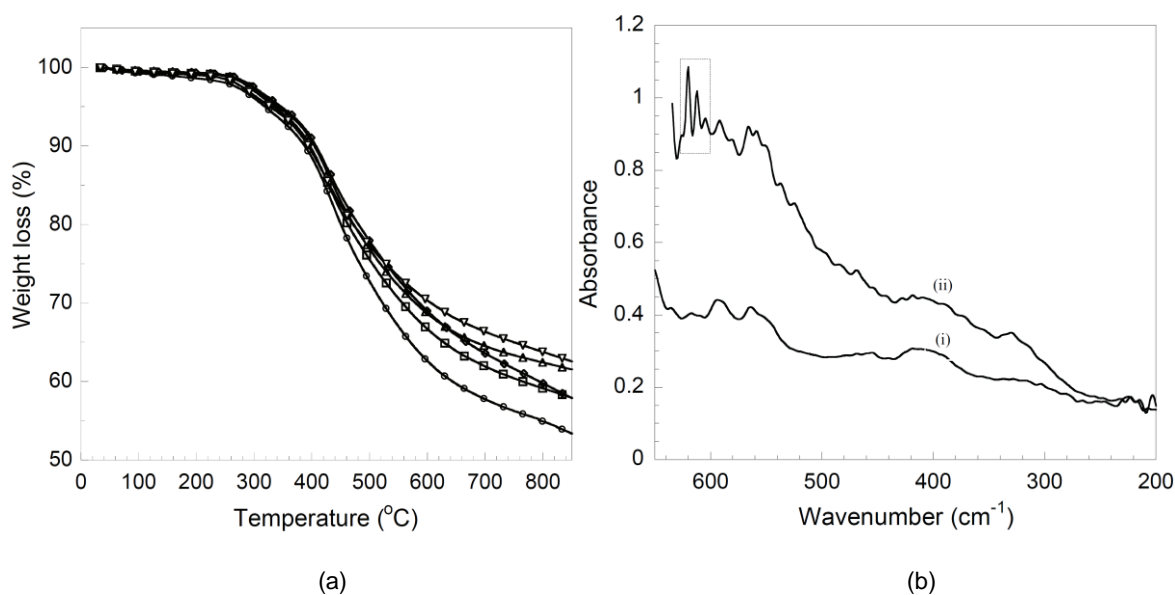


Figure 2: (a) TGA thermogram of BA-35x:BTDA (1:0.67)-based poly(benzoxazine-ester) copolymer filled with various nanoalumina contents (\circ) 0 wt%, (\square) 5wt%, (\diamond) 10 wt%, (\triangle) 15 wt%, (∇) 20 wt%, (b) poly(benzoxazine-ester) copolymer based on BA-35x:BTDA (1:0.67) (i), poly(benzoxazine-ester) copolymer filled with nanoalumina of 10 wt% (ii).

Effects of nanoalumina contents increased from 5 wt% to 30 wt% on thermal diffusivity value of the poly(benzoxazine-ester) composite films based on BA-35x:BTDA mole ratio of 1:0.67 are plotted in Figure 3. The thermal diffusivity increased nearly linearly, to a value of approximately $11.3 \times 10^{-8} \text{ m}^2/\text{s}$, while that of the BA-35x:BTDA (1:0.67)-based poly(benzoxazine-ester) copolymer film was about $9.8 \times 10^{-8} \text{ m}^2/\text{s}$. Then, the thermal diffusivity goes through a sharp increase to be $14.5 \times 10^{-8} \text{ m}^2/\text{s}$ for 30 wt% nanoalumina-filled poly(benzoxazine-ester) composite film. This behaviour indicated that these composites might form co-continuous structure. In addition, as the thermal conductivity is based on strong vibrational coupling between the particles for effective heat transfer through the contact, it can be concluded that good efficiency of contact between nanoalumina particles was achieved in the nanoalumina-filled poly(benzoxazine-ester) composite film.

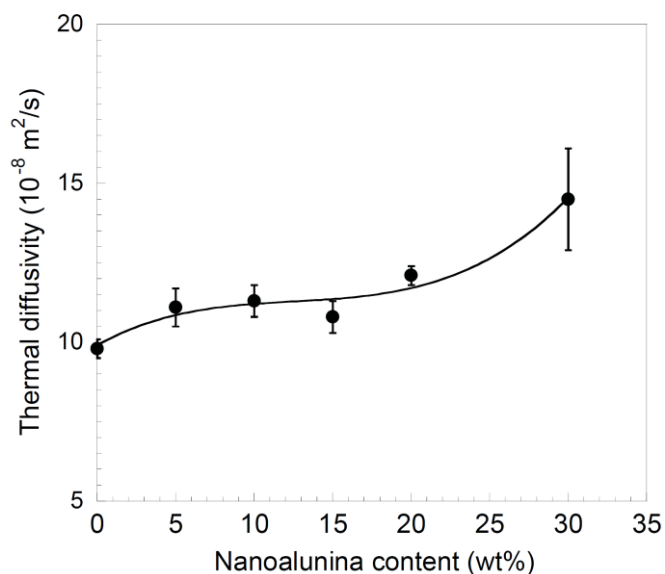


Figure 3: Thermal diffusivity vs. nanoalumina content for nanoalumina-filled poly(benzoxazine-ester) composite films

4. Conclusions

A series of a novel poly(benzoxazine-ester) copolymer films were prepared by blending BA-35x type benzoxazine monomer and BTDA, followed by thermal curing. The thermal properties of the polybenzoxazine were significantly enhanced by blending with BTDA due to ester group formation in the copolymer structures. Viscoelastic measurement and thermogravimetric analysis displayed that the presence of BTDA can also help improve modulus, glass transition temperature, and thermal stability of the polybenzoxazine. In case of nanoalumina-filled poly(benzoxazine-ester) composite films, the thermomechanical properties, thermal stability, and thermal diffusivity of the poly(benzoxazine-ester) copolymer films can be improved by addition of nanoalumina particles. Storage modulus of 4.11 GPa, glass transition temperature of 310 °C, and degradation temperature of 404 °C were obtained for the composite film with 15 wt% of nanoalumina, while thermal diffusivity of the composite film significantly increased to 14.5×10^{-8} m²/s as the nanoalumina content reached 30 wt%. Considering the high mechanical property, thermal stability, and thermal diffusivity of the nanoalumina-filled poly(benzoxazine-ester) composite films, they can potentially be used in the applications that require high stiffness and high thermal properties.

Acknowledgments

The authors would like to acknowledge the financial support from the Matsumae International Foundation, Japan (2012) and the University budget in the fiscal year 2012 (Contact grant no. 111/2555). Addition funding was provided by the Ratchadapiseksompot Endowment Fund of Chulalongkorn University. Prof. Shinji Ando is also acknowledged for providing us with the equipment, i.e., FTIR and TWA.

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