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Synergistic Improvement of Flame Retardancy and Mechanical Properties of Epoxy/Benzoxazine/Aluminum Trihydrate Adhesive Composites

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Abstract: Epoxy was blended with benzoxazine resin and aluminum trihydrate (ATH) additive to render flame retardancy while maintaining mechanical properties. The ATH was modified using three different silane coupling agents and then added to 60/40 epoxy/benzoxazine mixtures. The effect of blend compositions and surface modification on flame retardant and mechanical properties of the composites was investigated by UL94, tensile, and shear tests. Resin mixtures containing more than 40 wt% benzoxazine revealed a UL94 V-1 rating with enhanced tensile and shear strength. Upon addition of 20 wt% ATH to 60/40 epoxy/benzoxazine, a V-0 rating was achieved. The lowered tensile and adhesive properties of the composites in the presence of ATH were improved by modifying the ATH surface using silane coupling agents.

Keywords: adhesive; aluminum trihydrate; benzoxazine; flame retardancy; silane coupling agent

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1. Introduction

Under the increasing safety concerns, flame retardant adhesives attract enormous attention in the automotive, electronic, and construction industries. The adhesives are designed to provide thermal runaway protection and cell-to-cell bonding of battery systems in electric vehicles [1–3]. Regarding the electronic assemblies such as power conversion units and cooling devices, fire blocking characteristics through system design or component materials are required [4–6]. The thermal stability of organic resins determines the flame-retardant capability of adhesives. Although epoxy resins are the most widely used owing to their high strength and good dimensional stability, their flammable characteristic restricts their potential uses. Flame retardant adhesives in transportation and electronics allow composites to meet a V-0 rating during vertical burning tests (UL94). Benzoxazine possesses many desirable properties such as excellent thermal stability, low flammability, and near-zero shrinkage without releasing toxic products during cure [7–11]. The aromatic rings and nitrogen element in polybenzoxazine structure, and crosslinkable feature give them high heat resistance and good flame retardancy. However, a glassy state at room temperature necessitates high curing temperature and additional reactive diluents to expand a processing window. When the epoxy is blended with benzoxazine, the mixture is easy to handle and additionally the interlocked homogeneous structures after copolymerization exhibit good thermos-mechanical properties [12–16]. Despite many promises of the epoxy/benzoxazine blends, the flame retardancy is still unsatisfactory for industrial uses because of its intrinsic organic nature.

The use of flame-retardant additives is a simple and effective way of suppressing fire risk. Halogen-based substances reveal excellent fire resistance but generate toxic and corrosive gases during combustion. In the European Union (EU), halogenated flame retardants were prohibited in electronic display from March 2021. Recently, aluminum trihydrate (ATH) is widely used as a replacement because of its low cost and non-toxic gas emissions [17–22]. It undergoes endothermic dehydration upon heating above 180 °C, suppressing the flame spread and smoke emission]. In general, a considerable amount of ATH particles above 50 wt% needs to be added to meet the desired flame retardancy in industries due to relatively poor efficiency. Such high loading deteriorates the mechanical properties, processability, and long-term stability of the composites. Numerous attempts have been made to maximize flame retardancy without deteriorating mechanical properties, including the use of smaller ATH particles having large surface areas and combination with other flame retardants [23,24]. Surface modification is also a common approach to improving mechanical properties. Silane coupling agents having an organic and inorganic end is most frequently used [25–28].

In the present study, the epoxy resin was blended with the benzoxazine in order to enhance the fire and mechanical properties and then the ATH was added to achieve synergistic flammability. Physical property losses of the epoxy/benzoxazine/ATH composites have been ameliorated by surface modification of the ATH using three different silane coupling agents. Flammability and mechanical properties of epoxy/benzoxazine mixtures and epoxy/benzoxazine/ATH composites have been measured in relation to blending composition. UL94 burning test was carried out to determine the flame retardancies, while tensile and shear strength were measured for a mechanical test.

2. Materials and Methods

2.1. Materials and Sample Preparation

Epoxy with a reported viscosity of 250 mPa·s at 25 °C manufactured from Daicel Chemical Industries were blended with benzoxazine (P-d type, Shikoku Chemicals, Kagawa, Japan) at various compositions. Pure epoxy and its mixture with benzoxazine were thermally cured in presence of 50 wt% of curing agent (RIKACID MH-T, New Japan Chemical, Osaka, Japan) and 5 wt% accelerator (2E4MZ-CN, Shikoku Chemicals, Kagawa, Japan), respectively. Aluminum trihydrate (SG-10LSA, Sibelco, Antwerpen, Belgium) having average particle size of 3.3 μm was used as a flame retardant. Three kinds of silane coupling agents containing epoxy (KBM403), amino (KBM603), mercapto (KBM803) functional group, were supplied by ShinEtsu, Japan.

The coupling agent (1 g) was dissolved in 200 g ethanol and then stirred at 150 rpm for 10 min. After 100 g of ATH was slowly added, the mixtures were homogenized by mechanical stirring at room temperature and then reacted at 60 °C. The product was filtered and then washed with deionized water several times. Silane-treated ATH was dried at 90 °C in a convection oven for 12 hrs. Uniform mixtures containing epoxy, benzoxazine, and ATH were achieved using a conventional three roll mill (EXAKT 80E, EXAKT, Norderstedt, Germany) and then rotated at 100 rpm for 30 min in a vacuum bath to remove the residual bubbles. The homogeneous mixtures were stored in a refrigerator at -40 °C prior to use. The epoxy/benzoxazine resins were thermally cured at 175 °C for 60min.

2.2. Characterization

Tensile and adhesion tests of the adhesive composites were performed using a Universal Testing Machine (AG-50KNX, Shimadzu) according to ASTM D638 and ASTM D1002 standard specifications, respectively. Tensile strength was measured at a crosshead speed of 5 mm/min, while the shear strength was measured by pulling the aluminum plates (114 mm in length × 20 mm in width × 3mm in thickness) at a rate of 1.27 mm/min in which the overlap length was 20 mm. The surface of aluminum is cleaned using ethanol prior to applying the adhesives. The flame retardance of cured epoxy/benzoxazine mixtures and their composites with ATH was evaluated by UL94 vertical test, where the dimension of specimen is 127 mm in length × 12.7 mm in width × 3.2 mm in thickness. Thermogravimetric analysis (TGA, Model Pyris 1, Perkin Elmer) was used to characterize the thermal stability of epoxy/benzoxazine blends. Approximately 10 mg of samples was heated from 30 °C to 600 °C at a rate of 10 °C/min under air environment. Coefficient of thermal expansion (CTE) of adhesives was estimated from the amount of thermal expansion versus temperature using TMA instrument (Model 2940, TA Instrument). A sample placed on the TMA cell was heated from 20 °C to 150 °C using a heating rate of 5 °C/min. The viscoelastic behavior was probed in a sinusoidal tension mode using Pyris Diamond DMA (Perkin Elmer) technique. The cured film (200 mm in length × 6 mm in width × 0.3 mm in thickness) was heated from 25 °C to 280 °C at a heating rate of 2 °C/min under nitrogen environment. The frequency of the dynamic mechanical measurement was fixed at 1Hz.

3. Results

3.1. Thermal, Mechanical, Flammable Properties of Epxoy/Benzoxazine Mixtures

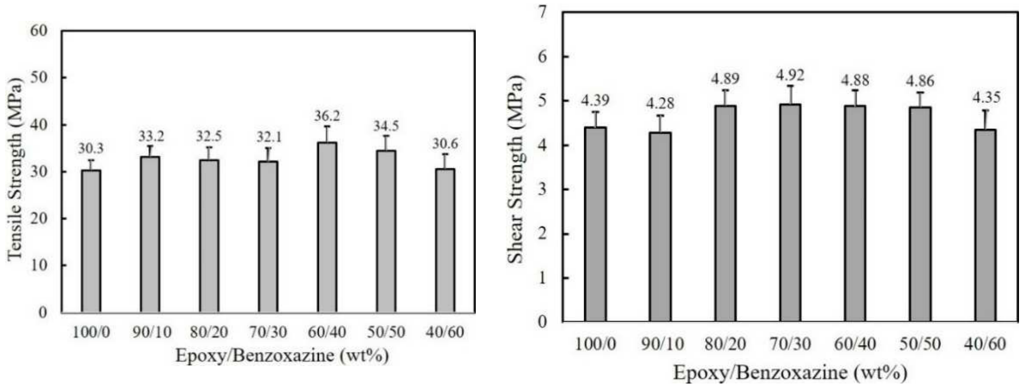
The thermal and mechanical properties of epoxy/benzoxazine mixtures are shown in Table 1. From the TGA measurement, pure epoxy reveals degradation temperature (T_d) at around 301 °C which corresponds to 5 wt% weight loss. Thermal degradation occurs at higher temperature with increasing the fraction of benzoxazine because of good thermal stability of benzoxazine. The glass transition temperature (T_g) determined from tan δ peak of DMA results slightly increases when epoxy is copolymerization with benzoxazine. The T_g of 50/50 epoxy/benzoxazine mixture is observed at around 163.0 °C. Thermal curing of epoxy/benzoxazine mixtures was conducted at 175 °C on the basis of the reaction peak of pure epoxy and thermal dehydration temperature of ATH. Considering the exothermic reaction of pure benzoxazine at around 250 °C, the T_g of the mixtures can be shifted to the higher temperature upon elevating curing temperature.

The coefficient of thermal expansion (CTE) of pure epoxy below (α_1) and above (α_2) the T_g is found to be 95 ppm/°C and 162 ppm/°C, respectively. When benzoxazine is blended with epoxy, the CTE values tend to decrease. The thermal stress may be suppressed by lowering the thermal expansion mismatch between the adhesives and the die. The storage modulus of neat epoxy at room temperature increases with the amount of benzoxazine resin, i.e., 4 GPa for pure epoxy to 6.2 GPa for 70/30 epoxy/benzoxazine. The reduced modulus at high benzoxazine content above 40 wt% may be attributable to reduced crosslinking density. Viscosity is one of the crucial criteria to determine the processibility of the adhesives. The viscosity of pure epoxy having approximately 250 mPa·s at 5 rpm increases significantly as benzoxazine content increases because pure benzoxazine is in a glassy state at room temperature. Generally, the viscosity of adhesives in the range of 8,000 to 30,000 cPs is recommended for dispensing purposes. Since the viscosity is expected to increase further upon adding ATH additives, the benzoxazine content in mixtures is limited.

Table 1. Composition-dependent thermal, mechanical properties of epoxy/benzoxazine mixtures.

Epoxy/Benzoxazine (wt/wt%)	T_d (°C)	T_g (°C)	CTE (ppm, °C^{-1})		Modulus (GPa)		Viscosity (mPa·s)
			α_1	α_2	25°C	250°C	
100/0	301	158.9	95	162	4.0	0.015	250
90/10	300	159.4	70	161	5.2	0.019	663
80/20	355	160.6	68	153	5.3	0.015	2,568
70/30	355	162.9	45	150	6.2	0.025	3,397
60/40	350	160.4	37	141	5.2	0.030	17,170
50/50	354	163.0	35	142	4.8	0.031	29,830

Figure 1(a) displays the tensile strength of pure epoxy and epoxy/benzoxazine blends. The benzoxazine loading is limited to 60 wt% due to high viscosity. The tensile strength of pure epoxy observed at around 30.3 MPa gradually increases upon the addition of benzoxazine and reaches the highest strength value of 36.2 MPa at 60/40 epoxy/benzoxazine composition. Tensile strength decreases to 34.5 MPa at 50 wt% and 30.6 MPa at 60wt%, respectively. At > 50 wt% benzoxazine, unreacted monomeric residues from benzoxazine increases at a given curing conditions. In addition, benzoxazine itself generally exhibits low crosslinking density compared to other thermoset resins. The lap shear strength results of various epoxy/benzoxazine mixtures on the aluminum (Al) substrates are shown in Figure 1(b). The adhesion strength of pure epoxy showing at around 4.39 MPa increases above 4.8 MPa with the addition of benzoxazine in a range of 20-50 wt%. The adhesion strength is closely associated with the ability of the adhesive to wet and spread onto the substrate surface as well as mechanical properties of the resins. As the viscosity of the mixtures increases in proportional to benzoxazine content, the wettability on Al surface may be interfered. The crosslinking density of the mixtures may also affect the adhesion strength.



(a) (b)

Figure 1. The variation of (a) tensile strength and (b) adhesion strength of epoxy/benzoxazine mixtures depending on blending compositions.

Table 2 presents the burning characteristics of epoxy/benzoxazine mixtures including a UL94 rating and dripping behavior. The mixtures containing less than 30 wt% benzoxazine completely burned after the first ignition and failed the flammability test. Highly flammable epoxy may have a dominant effect on the fire resistance at this composition. With further increase of benzoxazine content above 40 wt%, the combustion time, a sum of burning time after first and second ignition, is reduced to 175s for 60/40 and 71s for 50/50 epoxy/benzoxazine, indicative of having a V-1 rating. It is noticed that the fire resistance can be imparted when at least 40 wt% benzoxazine is added to epoxy. The epoxy/benzoxazine blend alone is still unsatisfactory in passing the commercial fire performance of a V-0 rating. The ATH is incorporated into the epoxy/benzoxazine mixtures.

Table 2. The UL94 results of epoxy/benzoxazine mixtures at various composition.

Epoxy/Benzoxazine (wt/wt%)	**Combustion time (s)**		**Dripping**	**Rating**
	after 1st ignition	**after 2nd ignition**		
100/0	burned	-	D	No rating
90/10	burned	-	D	No rating
80/20	burned	-	D	No rating
70/30	burned	-	D	No rating
60/40	175	0	N	V-1
50/50	71	0	N	V-1

3.2. Mechanical and Flammable Properties of Epoxy/Benzoxazine/ATH Composites

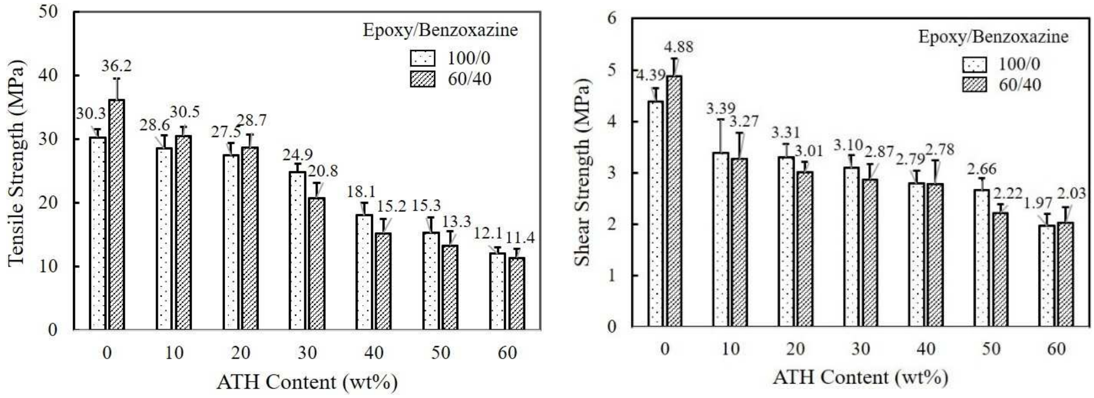
Table 3 shows the variation of thermal and mechanical properties of the 60/40 epoxy/benzoxazine mixture when ATH is incorporated. The T_g of epoxy/benzoxazine mixtures remains almost invariant regardless of ATH content, showing at around 160 ~ 162 ^oC. It implies that the crosslinking density of the mixture is not affected by the ATH. The coefficient of thermal expansion (CTE) values, α_1 and α_2, gradually decreases with the increase in ATH content because of the low CTE of inorganic ATH (15 ppm/^oC), whereby the expansion of the matrix is constrained. As the average inter-particle distance decreases with the incorporation of more particles, the loosely bound network gradually gets transformed into a tightly bound network. The reduction of α_2 value is more apparent, 141 ppm/^oC for epoxy/benzoxazine mixtures and 92 ppm/^oC for the mixture containing 40 wt% ATH. The storage modulus of epoxy/benzoxazine mixtures increases up to 8.4 GPa at 25 °C and 0.081 GPa at 250 °C, respectively when 40 wt% ATH is loaded. It is observed that the addition of inorganic materials improves the storage modulus but causes a decrease in tensile and adhesion properties.

Table 3. The effect of ATH addition on thermal and mechanical properties of 60/40 epoxy/benzoxazine mixtures.

ATH Content (wt%)	T_g (°C)	CTE (ppm, °C^{-1})		Modulus (GPa)	
		α_1	α_2	25°C	250°C
0	160.4	37	141	5.2	0.030
10	162.4	33	133	7.2	0.045
20	160.0	32	130	8.4	0.063
30	159.2	32	109	8.4	0.065
40	161.6	31	92	8.1	0.081

From the thermal and mechanical behaviors, the 60/40 epoxy/benzoxazine mixture was selected as the optimal composition. Figure 2(a) shows the variation of tensile strength of neat epoxy and 60/40 epoxy/benzoxazine mixture when the ATH in different amount is added. Tensile strength of pure epoxy and epoxy/benzoxazine mixture exhibiting 30.3 and 36.2 MPa is reduced dramatically as ATH content increases, exhibiting 12.1 and 11.4 MPa at 60 wt% ATH. No reinforcement effect is observed for both epoxy and epoxy/benzoxazine mixtures. Reduced strength value may be attributable to the incompatibility between adhesive resin and ATH additive. Adhesives become harder as the amount of ATH increases, resulting in low elongation at the break.

The effect of ATH content on the adhesion (or shear) strength of pure epoxy and 60/40 epoxy/benzoxazine blends was investigated using aluminum (Al) adherend. The shear strength is shown in Figure 2(b). The shear strength of pure epoxy and epoxy/benzoxazine mixtures indicates that the addition of ATH lowers the strength of the matrix-Al interfacee, showing about 55% and 58% reduction at 60 wt% ATH loading. The strength of an adhesive joint is closely related to the ability of the adhesive to wet and spontaneously spread onto the Al surface. The addition of ATH particles increases the viscosity of the resin, which in turn hampers the flowability and wetting in a bond.



(a) (b)

Figure 2. The variation of (a) tensile strength and (b) adhesion strength of pure epoxy and 60/40 epoxy/benzoxazine mixtures upon addition of ATH.

The flame retardancy of the epoxy/benzoxazine mixtures with respect to ATH content is summarized in Table 4. Pure epoxy is highly combustible and thus the flame spreads to the holding clamp rapidly after ignition. When ATH is added to epoxy, the cotton indicator is still ignited by melt drips up to 30 wt%. At 40 wt% ATH, the fire stops within the 60s, and ignition of the cotton by dripping is no longer observed, exhibiting a V-1 rating. At 50 wt%, the composite finally reaches a V-0 rating. The flammability behavior clearly indicates that pure epoxy needs at least 50 wt% ATH to

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pass the required fire performance. However, such high ATH loading deteriorates tensile and adhesion strength. When 60/40 epoxy/benzoxazine mixture exhibiting a V-1 rating is combined with ATH, the burning time lessened to 70s at 10 wt%, 35s at 20 wt%, and 25s at 30 wt% ATH. This result indicates that the mixture can pass the V-0 rating even at 20 wt% ATH loading. The mixture containing 50 wt% benzoxazine shows a V-0 rating at 10 wt% of ATH with a reduced combustion time of 40s, and no ignition occurs at 30 wt% ATH. This result clearly indicates that the flame can be retarded effectively by the combined use of benzoxazine resin and ATH filler.

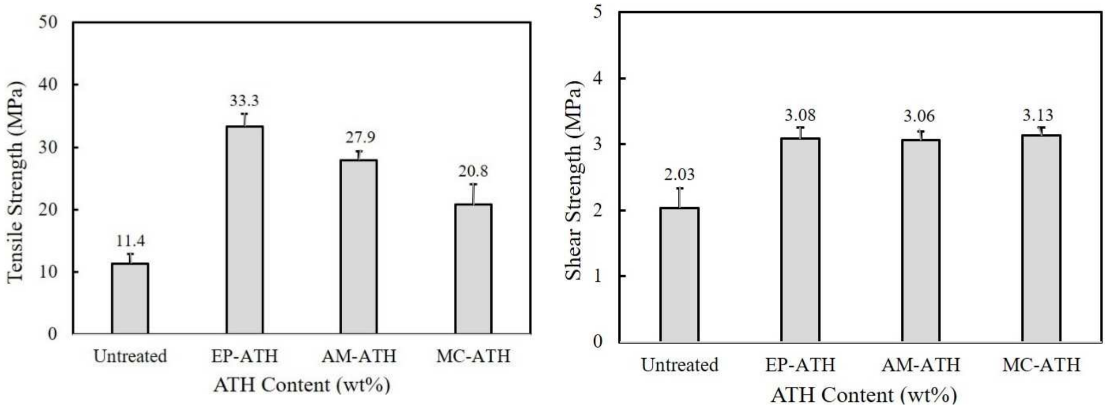
Table 3. The effect of ATH addition on thermal and mechanical properties of 60/40 epoxy/benzoxazine mixtures.

Epoxy/Benzoxazine (wt/wt%)	ATH Content (wt%)	Combustion time (s)		Dripping	Rating
		after 1st ignition	after 2nd ignition		
100/0	10	burned	-	D	No rating
	20	burned	-	D	No rating
	30	burned	-	D	No rating
	40	0	53	N	V-1
	50	0	0	N	V-0
	60	0	0	N	V-0
60/40	10	0	70	N	V-1
	20	0	35	N	V-0
	30	0	25	N	V-0
	40	0	0	N	V-0
	50	0	0	N	V-0
	60	0	0	N	V-0
50/50	10	0	40	N	V-0
	20	0	20	N	V-0
	30	0	0	N	V-0
	40	0	0	N	V-0
	50	0	0	N	V-0
	60	0	0	N	V-0

3.3. Effect of Surface Modification on Mechanical Properties of Epoxy/Benzoxazine/ATH Composites

It was observed that the incorporation of ATH into the 60/40 epoxy/benzoxazine mixture led to a significant reduction in tensile and adhesion strength. The ATH was modified using three different silane coupling agents containing epoxy (EP), amino (AM), and mercapto (MC) functional groups. Figure 3(a) shows the tensile strength of 60/40 epoxy/benzoxazine blends when 60 wt% ATH is incorporated. All the coupling agents show high tensile strength compared to untreated ATH, in the order of EP-ATH > AM-ATH > MC-ATH. The strength value of the composite filled with EP-ATH is observed at around 33.3 MPa, which is about three times higher than that of the untreated ATH.

The composites containing surface-modified ATH also exhibit higher adhesion strength (Fig. 3b). Regardless of the functional groups of coupling agents, the composites prepared using modified ATH show the shear strength above 3 MPa, about 1 MPa higher than that of untreated ATH composites. From the tensile and adhesion strength results, it is inferred that surface modification using silane coupling agents is an effective way to prevent the deterioration of the mechanical properties of adhesives. The improvement is mostly attributed to a better dispersion of surface-modified ATH and strong adhesion between the ATH and matrix. The introduction of a coupling agent on the ATH surface may increase an affinity to the matrix and suppress the generation of voids and cracks at the interface.



(**a**) (**b**)

Figure 3. Comparison of (a) tensile strength and (b) adhesion strength of epoxy/benzoxazine/ATH composites after surface modification using silicone coupling agents having epoxy, amino, and mercapto functional groups.

4. Conclusions

The benzoxazine and ATH were added to the epoxy and then the thermal, mechanical, and flame-retardant behaviors of the composites have been examined. The blends of epoxy and benzoxazine exhibited high degradation temperature, low CTE, high tensile strength, and storage modulus. The mixtures containing 40 wt% benzoxazine passed the UL94 V-1 rating while maintaining good tensile and adhesion strength. The amount of benzoxazine in mixtures was limited because of the narrow processing window and low crosslinking density. The ATH provided a satisfactory flame retardancy. The effective amount of ATH required to achieve a V-0 rating for pure epoxy was 50 wt%. Higher ATH loading led to a pronounced decrease in tensile and shear strength of the composites. When ATH was added to the 60/40 epoxy/benzoxazine, a V-0 rating could be achieved even at 20 wt% without much sacrificing the mechanical properties. The combined use of ATH and benzoxazine showed noteworthy synergism in terms of flame retardance and mechanical properties. The lower tensile and shear strength of the ATH composites can be improved by surface modification using a silane coupling agent.

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