Preparation and Performance of Aluminum Borate Whisker–Reinforced Epoxy Composites. I. Effect of Whiskers on Processing, Reactivity, and Mechanical Properties

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ABSTRACT: Aluminum borate ($Al_{18}B_4O_{33}$) whisker–reinforced composites based on a epoxy resin, which was made up of a trifunctional epoxy resin, TDE 85, and methyl nadic anhydride (MNA), were prepared, and the effects of the whiskers on the processing, reactivity, and typical mechanical properties of the composites were investigated. Two coupling agents, aluminate (DL411A) and borate (BE4), were used to surface treat the whiskers. Results show that the addition of the whiskers does not change the reactivity of the matrix, while increasing the viscosity of the resin, but when the whisker content is less than 5 wt %, the increased viscosity does not obviously influence the processing characteristics of the resin. Mechanical properties are greatly dependent on the chemistry and concentration of the coupling agent for treating the whiskers. A good coupling agent, which has good interaction with the whiskers and the matrix, can effectively improve the compatibility between the whiskers and the matrix, and thus result in great improvement of mechanical properties. BE4 proved to be better than DL411A for treating the whiskers. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1950–1954, 2004

Key words: aluminum borate whiskers; epoxy; compatibility; composites; thermosets

INTRODUCTION

Since the first epoxy resin patents were granted in the 1930s and 1940s, the properties of epoxy resins, such as excellent chemical resistance, very good adhesion, and ease of handling and processing, have been used in many applications including surface coatings, adhesives, castings, and laminates.[1–4] However, because of increasing demand for high-performance materials, many modifications have been conducted to upgrade the properties of epoxy resins, including the use of various reinforcements such as fibers and fillers, for example. Whisker-reinforced polymeric composites have attracted considerable interest of scientists and engineers recently because whiskers are generally recognized as being free from internal defects, such as dislocations, attributed to their small diameters, and thus the yield strength of whiskers tends to approach the maximum theoretical value.[5–8] The increasing property/price ratio of whiskers and good processing characteristics of polymers also greatly promote the development of whisker-reinforced polymeric composites. Aluminum borate ($Al_{18}B_4O_{33}$) whiskers are a relatively new kind of whiskers, developed in the 1980s, which have an attractive property/price ratio.[9] As is known, inorganic and organic materials generally are not compatible, and composites based on them generally cannot obtain desirable properties without compatibilization between the reinforcement and the matrix. Surface treatment of reinforcements, by use of a suitable coupling agent that has good interaction with both the reinforcement and the matrix, has been a widely used technique. In this article, a commercial aluminate (DL411A) and a borate (BE4) synthesized by our research group[10] were selected to treat $Al_{18}B_4O_{33}$ whiskers. Three composites based on TDE 85 epoxy/MNA resin (a commercial resin with good processing characterization and cured properties) and untreated or treated $Al_{18}B_4O_{33}$ whiskers were prepared, and their processing, reactivity, and typical mechanical properties were investigated.

EXPERIMENTAL

Materials

The epoxy resin used was TDE 85, a trifunctional epoxy resin based on 1,2-diformic acid cyclohexane (epoxide value = 0.86; Tianjing Jingdong Chemical Factory, China). Methyl nadic anhydride (MNA) and

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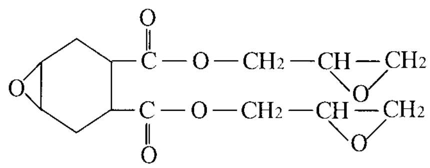
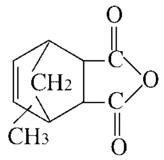
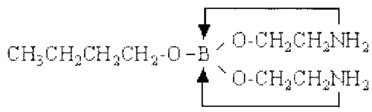


TDE 85



MNA



BE-4

Scheme 1 Chemical structures of TDE 85, MNA, and BE4.

2-ethyl-4-methyl imidazole were purchased from the Institute of Tianjing Synthesis Materials (China). $Al_{18}B_4O_{33}$ whiskers were kindly supplied by Qihai Haixing Science and Technology Development Ltd. (China). Aluminate (DL411A, a patented product[11]) was bought from Nanjing Shuguang Chemical Factory(China). A borate (BE4) was synthesized by our research group.[10] Acetone and anhydrous ethanol were supplied by Xi'an Chemical Factory (China). The chemical structures of TDE 85, MNA, and BE4 are shown in **Scheme 1**. All the materials involved in this work were industrial grade and used as received without any further purification.

Surface treatment of whiskers

$Al_{18}B_4O_{33}$ whiskers were dried at 105–110°C, then added into appropriate quantities of anhydrous ethanol solution of BE4 or acetone solution of DL411A with thorough stirring to form a homogeneous whisker solution. After that, the whisker solution was evaporated to remove the solvent at room temperature for 8 h, then subsequently dried at 80–90°C for 2 h. The resultant whiskers were designated as $Al_{18}B_4O_{33}$ (BE4) and $Al_{18}B_4O_{33}$ (DL411A), respectively.

Preparation of neat epoxy resin

TDE 85 (100 g) and MNA (150 g) were charged to a flask equipped with a mechanical stirrer and thermometer, after which 1 wt % 2-ethyl-4-methyl imidazole was added to the mixture with stirring. The mixture was then degassed in a vacuum oven at 50–60°C under 660 mmHg for 15 min. After that, the mixture was cast into a glass mold for curing and postcuring by use of the following procedures:

Curing: 120°C/2 h + 140°C/2 h + 160°C/2 h + 180°C/2 h
Postcuring: 200°C/5 h

Preparation of Ep/$Al_{18}B_4O_{33}$ composites

TDE 85 (100 g) and MNA (150 g) were charged to a flask equipped with a mechanical stirrer and thermometer, after which 1 wt % 2-ethyl-4-methyl imidazole was added to the mixture with stirring as a catalyst. Preweighed $Al_{18}B_4O_{33}$ whiskers were then added to the mixture with thorough stirring. Thereafter the mixture was degassed in a vacuum oven at 50–60°C under 660 mmHg for 15 min. Finally, the mixture was subjected to viscosity, gel, and contact measurements, or cast into a glass mold for curing and postcuring according to procedures described above. The obtained composite was designated as Ep/$Al_{18}B_4O_{33}$.

Two other kinds of composites were prepared by a method similar to that described above except that the whiskers used were $Al_{18}B_4O_{33}$ (DL411A) or $Al_{18}B_4O_{33}$ (BE4), respectively. The resultant composites were designated as Ep/$Al_{18}B_4O_{33}$ (DL411A) or Ep/$Al_{18}B_4O_{33}$ (BE4), respectively.

Measurements

Viscosities of samples were measured with an NDJ 79 viscometer (Experimental Instrument Co. of Tongji University, Shanghai, China) at 25°C according to GB 7193.1-87.

Gel time was measured on a temperature-controlled hot plate by a standard knife method: the time required for the resin to stop stringing and become quite elastic was taken as the gel time at a fixed temperature.

Contact angle was tested by a JY-82 contact angle tester (Chengde Experimental Instrument Co., Hebei, China). Samples were prepared by pressing whiskers into a thin film by use of a powder press. TDE 85 epoxy was used as the reference.

Tensile properties and impact strength were tested according to GB/T8814-1998 and GB/T2571-1995, respectively.

RESULTS AND DISCUSSION

Effects of coupling agents on the wettability of whiskers to the matrix

To obtain good interfacial adhesion between the matrix and whiskers, whiskers should be wetted by the

TABLE I
Contact Angle Between Whiskers and TDE 85 Epoxy

Whisker	Reference	Contact angle (°)
$Al_{18}B_4O_{33}$	TDE 85	36.4
$Al_{18}B_4O_{33}$ (BE4)	TDE 85	24.1
$Al_{18}B_4O_{33}$ (DL411A)	TDE 85	26.0

matrix. The contact angle is usually used to characterize the quality of the wettability. Table I lists the contact angles between epoxy and different surfaced-treated or untreated whiskers by use of various coupling agents. It can be seen that the contact angles between the epoxy and surfaced-treated whiskers are much lower than those between epoxy and untreated whiskers, indicating that wettability between the matrix and whiskers is improved by using a coupling agent. For the three whiskers used in this study, BE4-treated whiskers have the best compatibility with the epoxy.

Effect of $Al_{18}B_4O_{33}$ whiskers on the reactivity of the matrix

Generally, the addition of fillers with small size into the matrix may change the reactivity of the matrix system. Whiskers have smaller size than common fillers; moreover, they are usually acidic because of the existence of –OH groups on their surface. The reactivity of a resin can be greatly changed under acid conditions. Therefore, it is necessary to study the effect of $Al_{18}B_4O_{33}$ whiskers on the reactivity of a TDE 85/MNA system. Gel times, at various temperatures, are widely used to evaluate the reactivity of a resin. From Table II, it can be seen that the addition of $Al_{18}B_4O_{33}$ whiskers does not change the gel times within the whole temperature range, indicating that similar curing procedures can be used to prepare neat resin and $Al_{18}B_4O_{33}$ whisker–reinforced composites.

Effect of $Al_{18}B_4O_{33}$ whiskers on processing characteristics of the matrix

A suitable viscosity is necessary to process thermosets with high quality. Figure 1 shows the dependency of the viscosity on whisker content for Ep/$Al_{18}B_4O_{33}$

TABLE II
Gel Time of TDE 85/MNA, Ep/$Al_{18}B_4O_{33}$ System at Various Temperatures

	Gel time (min) at				
Component	80°C	100°C	120°C	140°C	160°C
TDE 85/MNA	120	24	8	5	2
Ep/$Al_{18}B_4O_{33}$ (95/5 wt %)	125	24	9	5	2

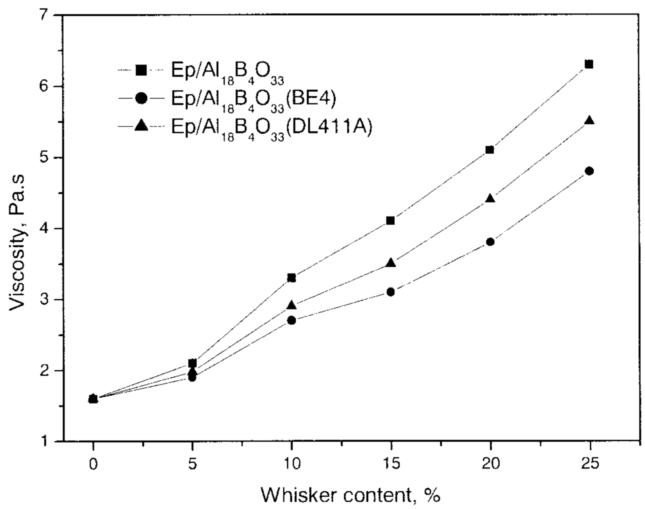


Figure 1 Variation of viscosity on whisker content of composites.

composites. Apparently, the viscosity tends to increase with increasing whisker content; furthermore, composites with untreated whiskers have higher viscosity than those with DL411A- or BE4-treated whiskers under the same whisker content, and the Ep/$Al_{18}B_4O_{33}$ (BE4) composite has the lowest viscosity, which may be attributed to the surface treatment of whiskers improving the compatibility between the matrix and whiskers and thus reducing the frictional force found between polymer and whiskers. Figure 1 also suggests that, when the whisker content is low, such as 5 wt %, the viscosities of Ep/$Al_{18}B_4O_{33}$ and/or Ep/$Al_{18}B_4O_{33}$ (BE4) composites are still low, and thus the composites still have processing characteristics similar to those of the pure resin system. However, when the whisker content reaches 15 wt %, viscosities of the composites are about 3.9 and 3.0 times that of the pure resin, respectively, Actually, when the content is as high as 50 wt %, the blending of whiskers and epoxy becomes difficult, and thus it is difficult to prepare composites with good quality.

Effect of coupling agent on typical mechanical properties of composites

Table III summarizes the typical mechanical properties of composites. Properties of the neat matrix are also listed for comparison. Results show that the mechanical properties of composites are closely related to the coupling agents, including their chemistries and concentrations. The addition of whiskers (both surface-treated or untreated) leads to a sharp enhancement of the modulus but a decrease in strain-at-break. This is a typical behavior of short-fiber and filler-reinforced polymer composites, but the influence is closely related to the chemistry of the coupling agent,

TABLE III
Typical Mechanical Properties of Epoxy Resin and Composites Containing Various 5 wt % $Al_{18}B_4O_{33}$ Whiskers

Material	Concentration of coupling agent (%)	Tensile			Impact strength (kJ/m^2)
		Strength (MPa)	Modulus (GPa)	Strain-at-break (%)	
TDE 85/MNA	—	78.2	2.9	3.0	9.1
Ep/$Al_{18}B_4O_{33}$	—	70.5	3.1	1.8	6.1
Ep/$Al_{18}B_4O_{33}$ (DL411A)	1	81.7	3.2	1.9	11.5
	2	86.1	3.5	2.2	13.8
	3	82.3	3.3	2.0	8.7
Ep/$Al_{18}B_4O_{33}$ (BE4)	1	82.2	3.3	2.0	12.1
	2	85.6	3.5	2.1	12.0
	3	88.0	3.6	2.3	14.2
	4	86.1	3.4	2.2	13.0

that is, Ep/$Al_{18}B_4O_{33}$ (BE4) composites have the highest modulus and strain-at-break, whereas Ep/$Al_{18}B_4O_{33}$ composites have the lowest values.

The above-noted effect of coupling agent on mechanical properties of composites can be seen more clearly from the impact and tensile strength of composites: the incorporation of untreated whiskers greatly reduces the impact strength and tensile strength, but the introduction of surface-treated whiskers, under the optimum concentration of the coupling agent, can effectively increase both the tensile and impact strengths of the resin. The improved efficacy of the coupling agents is related to their chemistry and is in the following order: BE4 > DL411A. For BE4, its central boron atom leads to good physical absorption on $Al_{18}B_4O_{33}$ whiskers; meanwhile, its –OC_4H_9 groups can react with –OH groups on whisker surfaces. On the other hand, –NH_2 groups in the BE4 molecule can react with epoxy groups of the resin, and thus BE4 has good physical and chemical interactions with both the matrix and whiskers. In the case of DL411A, no active groups exist in its molecular structure: its interaction with epoxy results only from the physical tangle of their hydrocarbon links, whereas the interaction of DL411A with whiskers results from the physical absorption of aluminum atoms in both DL411A and whiskers. Obviously, the interactions of BE4 with the matrix and whiskers are stronger than those of DL411A with the matrix and whiskers. This, in turn, results in better interfacial bonding between the matrix and $Al_{18}B_4O_{33}$ (BE4) than that between the matrix and $Al_{18}B_4O_{33}$ (DL411A), and thereby the Ep/$Al_{18}B_4O_{33}$ (BE4) composite has better mechanical properties than those of the Ep/$Al_{18}B_4O_{33}$ (DL411A) composite.

As described above, the mechanical properties of composites are also related to the concentration of the coupling agent used. There is an optimum concentration because, when the concentration is lower than the optimum value, the molecules of the coupling agent cannot completely cover the surfaces of whiskers. On the other hand, if the concentration is higher than the optimum value, more than one layer of coupling agent molecules covers the surfaces of whiskers, thus reducing the interactions of coupling agent with both whiskers and the matrix. For example, the coupling agent's inner layer, which has physical or chemical interactions with whiskers, cannot effectively react with the matrix, and the coupling agent's outer layer, which has physical or chemical interactions with the matrix, cannot have effective action with whiskers. Therefore, there is an optimum concentration of the coupling agent.

Effect of whisker content on mechanical properties of composites

Based on Table III, 2 wt % DL411A and 3 wt % BE4 were selected to treat $Al_{18}B_4O_{33}$ whiskers. The variation of mechanical properties with whisker content, for both kinds of composites, was investigated and compared. As shown from Figure 2 the tensile strength tends to increase with increasing surface-treated whisker content, but decreases with increasing

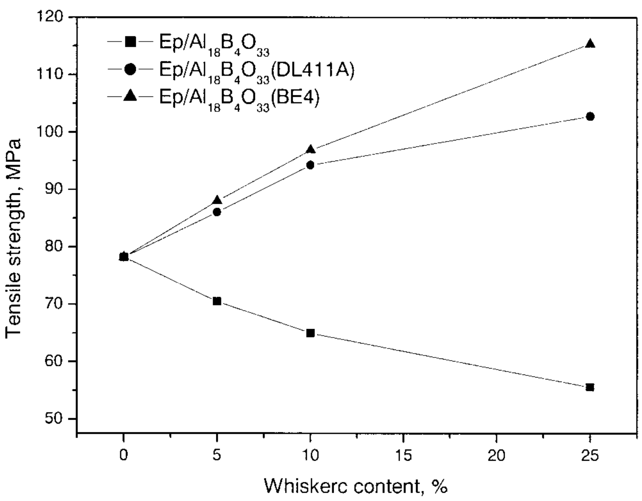


Figure 2 Tensile strength versus whisker content for three Ep/$Al_{18}B_4O_{33}$ composites.

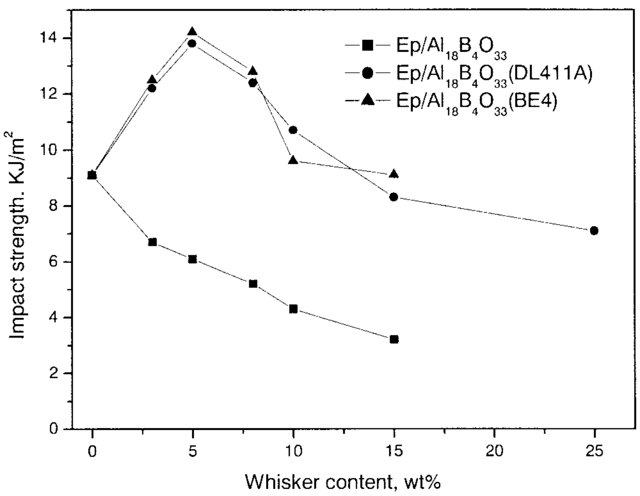


Figure 3 Impact strength versus whisker content for three $Ep/Al_{18}B_4O_{33}$ composites.

surface-untreated whisker content. In addition, it also can be seen from Figure 2 that the $Ep/Al_{18}B_4O_{33}$ (BE4) composite has much higher tensile strength than that of the other two composites, and composites with surface-untreated whiskers have the lowest tensile strength. The reduction in tensile strength, of the composites based on untreated whiskers, resulted from the agglomeration of untreated whiskers. These agglomerates were considered to be mechanical weak points because of poor wetting of whiskers by the matrix; therefore good dispersion of whiskers in the matrix and proper interfacial bonding are necessary for composites to obtain good properties because they allow better shear stress transfer between fillers and matrix, thereby effectively improving the mechanical properties of composites.

Figure 3 describes the relationship of impact strength of composites with whisker content. The impact strength tends to decrease with the addition of untreated whiskers because of the poor interfacial bond between the polymeric matrix and whiskers, whereas the incorporation of $Al_{18}B_4O_{33}$ (BE4) and $Al_{18}B_4O_{33}$ (DL411A) whiskers increases the impact strength of the matrix and, when the whisker content is 5 wt %, the impact strength of $Ep/Al_{18}B_4O_{33}$ (DL411A) and $Ep/Al_{18}B_4O_{33}$ (BE4) composites reach their highest values, which are 1.56 and 1.50 times that of the matrix.

Tjong et al.[12] investigated the mechanical properties of potassium titanate whisker–reinforced PA-6 composites. They reported that the impact strength initially decreased with increasing whisker content, but appeared to increase slightly when the whisker content reached 35 wt %. Avella et al.[13] reported that the incorporation of 20 wt % silicon carbide whiskers in PP led to a substantial increase in impact parameters, including the critical stress intensity factor and the critical strain energy release rate.

CONCLUSIONS

Composites based on the TDE 85/MNA system and $Al_{18}B_4O_{33}$ whiskers were prepared and the effects of whiskers on processing, reactivity, and typical mechanical properties were investigated. Results show that the addition of the whiskers does not change the reactivity of the matrix, but does increase the viscosity of the resin. When the whiskers content is less than 5 wt %, however, the increased viscosity does not obviously influence the processing characteristics of the resin. Mechanical properties indicated that the whiskers should be surface treated to improve the compatibility between the matrix and whiskers, and thereby effectively increase the tensile strength and impact strength of composites; otherwise, the incorporation of untreated whiskers sharply decreases the impact strength of composites.

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