Performance of Aluminum Borate Whisker Reinforced Cyanate Ester Resin

Yusheng Tang, Guozheng Liang, Zengping Zhang, Jing Han

Applied Chemical Department, School of Science, Northwestern Polytechnical University, Xi'an, Shaanxi 710072 People's Republic of China

Received 29 June 2006; accepted 22 October 2006
DOI 10.1002/app.26118
Published online 7 September 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Aluminum borate whisker (AlBw) treated with γ-methacryloxypropyltrimethoxy silane (KH550) and borate ester (BE4) was adopted to modify bisphenol A dicyanate/epoxy resin (BADCy/E-51) system, in this article. The influence of coupling agent and content of whisker on reaction activity were investigated by gel time and differential scanning calorimeter (DSC) and the results showed that addition of whisker enhances reaction activity of BADCy/E-51 system slightly. The dispersion of whisker in matrix and reinforcement mechanism was investigated by scanning electron microscope (SEM). Results reveal that whisker treated with BE4 had better dispersing than that treated with KH550 in resin. The thermal stability, mechanical properties, and hot–wet resistance of AlBw/BADCy/E-51 resin system were also studied. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 4131–4137, 2007

Key words: cyanate ester resin; whisker; reinforce; properties

INTRODUCTION

Currently, the association of the very light high-performance thermosetting polymers matrix composite, the thermal stability, and the good mechanical material properties allow structures of great dimensions to be much lighter. The current concerns of the military aviation that has contributed a large share in the development of these materials are on one hand to extend the lifetime in extreme environments and on the other hand to reduce costs by simplifying the manufacture of parts. Indeed, the use of high-performance thermosetting polymers particularly concerns manufacturers in aeronautic and spatial areas.

Over the last decade, cyanate ester (CE) has become established as a new and unique class of high-performance thermosetting resin for use as prepregs and matrices, because they have low dielectric loss properties, low water absorption, excellent heat resistance, and low volume shrinkage.[1] It is well documented that cyanate ester may suffer from brittleness because of the high crosslink density generated during cure, and several approaches have been developed to increase the impact resistance, the fatigue resistance, and the fracture toughness of the cured cyanate ester resins. Such approaches include blending with rubber and thermoplastic, copolymerization with epoxy resin, and formation interpenetrating network (IPN).[2–6]

Correspondence to: G. Liang (lgzheng@nwpu.edu.cn).

Journal of Applied Polymer Science, Vol. 106, 4131–4137 (2007)
© 2007 Wiley Periodicals, Inc.

Recently, whisker is adopted to prepare polymer matrix composites to enhance the toughness of polymer. Whiskers are short, fiber-shaped, single crystals with high perfection and very large length-to-diameter ratios. Owing to its perfect crystal structure, the tensile strength of a whisker is extremely high and close to the binding force of adjacent atoms.[7–13]

In the present article, the aluminum borate whisker (AlBw)/cyanate ester/epoxy resin systems were prepared and the mechanical properties and hot–wet stability of them were investigated. The effects of whisker-surface modification and whisker content on the properties were discussed. The microstructure of the system was revealed using a scanning electron microscope (SEM). The relationship between the microstructure and the properties was proposed.

EXPERIMENTAL

Raw materials

The cyanate ester resin, AroCy B10, a bisphenol A dicyanate resin (BADCy) used in this study was synthesized by our group. The epoxy resin, E-51 (epoxy equivalent weight, 0.51), a diglycidyl ether of bisphenol A was supplied by Epoxy Resin Corp. of Wuxi, China. Plain glass weave, Ew210, silane treated E-glass fabric with a thickness of 2 mm, (Glass Fiber Academe of Nanjing, China), was used without surface treatment. γ-Methacryloxypropyltrimethoxy silane (KH550) used as coupling agent was supplied by Nanjing Shuguang chemical plant, (Nanjing,

TABLE I
Properties of AlBw Whisker

Properties	Datum
Length (μm)	10–20
Diameter (μm)	0.5–1
Max operating temperature (°C)	1200
Density (g/cm^3)	2.93
Apparent density (g/cm^3)	0.01–0.05
Tensile strength (GPa)	8
Elastic modulus (GPa)	400
Coefficient of thermal expansion (%/°C)	4.2×10^{-6}

China). The other coupling agent is borate ester (BE4), was synthesized by our group. The whiskers used in this work are aluminum borate (AlBw) supplied by Qinghai Haixing Co., (Xining, China). Some properties of AlBw whisker are shown in Table I.

After being dried under 105–140°C for 4 h, aluminum borate whisker (AlBw) is mixed with borate ester anhydrous ethanol solution and silane acetone solution, respectively. The solutions including whisker have been stirred 1 h on magnetic force stirrer followed by drying for 8 h at room temperature and 2 h at 80–90°C.

Preparation of modified resin

Modified resins were prepared by blending BADCy and E-51 with AlBw whisker. Various resin systems with AlBw whisker and coupling agent contents are shown in Table II. A typical procedure for preparing modified resin was as following. The blend of AlBw whisker, BADCy resin, and E-51 resin was heated to 100°C and put into preheated clean molds. The resin was degassed at 100°C in a vacuum oven, cured following the following procedure: 130°C/2 h + 150°C/2 h + 180°C/2 h + 200°C/2 h, then slowly cooled to room temperature. The cured resin was demolded and post cured at 220°C for 4 h in an oven.

Testing

Gel time

The gel time of resins was determined with a standard hot-plate with a temperature controller. The resins were spread on the surface of the hot plates preheated to different temperatures. The time required for the resin to stop legging and become elastic is called the gel time.

Mechanical properties

Mechanical properties of the cured resins were determined with a Shimadzu autograph AGS-500B universal testing machine according to ASTM E-399.

Thermal analysis

Differential scanning calorimeter (DSC, Perkin-Elmer DSC-7) measurements were made at a scan rate of 10°C/min with 4–6 mg samples in a nitrogen atmosphere.

Heat deflection temperature (HDT) is carried out to determine the thermomechanical behavior of matrix systems. The heat deflection temperature of the samples was tested as per ASTM D 648-72 that defines HDT of a test specimen as the temperature at which it has a 0.25 mm deflection under a given load.

The thermal stability of the cured hybrid resin was test by thermal gravimetric analysis (TGA). Thermal stabilities of cured hybrid resin under nitrogen or air were tested using a TGA Q50 Instrument (TA Instruments). Samples (15–25 mg) were loaded in platinum pans a ramped to 900°C (10°C/min/N_2). The N_2 flow rate was 60 mL/min.

Hot–wet resistance

The hot–wet resistance of cured resins and composite was determined by placing samples into boiling distilled water for various lengths of time, removing and wiping off the sample with a dry cloth, and weighing the sample to the nearest 0.001 g immediately. Then, the value of water absorption was calculated according to ASTM D 570-81. The heat distortion temperature testing was performed in silicon oil at heating rate of 2°C/min according to GB 1663-79. The heat distortion temperature corresponds to a distortion of 0.32 mm of specimen.

Scanning electron microscope

The cured resins after impact and flexural test were fractured in liquid nitrogen, and subsequently examined in a scanning electron microscope (SEM) (JEOL JSM model 820). The fractured surfaces were coated with a thin layer of gold prior to SEM examination.

TABLE II
The Compositions of Modified Resin Systems (wt %)

Symbol	BADCy	E-51	AlBw	BE4	KH550
A	95	5	0	0	0
B1	95	5	5	0	0
B2	95	5	8	0	0
E2	95	5	5	2	–
E4	95	5	5	4	–
E6	95	5	5	6	–
E8	95	5	8	4	–
E10	95	5	10	4	–
K2	95	5	5	–	2
K4	95	5	5	–	4
K5	95	5	5	–	6
K8	95	5	8	–	4

RESULTS AND DISCUSSION

Reaction activity of BADCy/E-51/whisker system

The relationships between gel time and temperature of BADCy/E-51/AlBw system and BADCy/E-51 system are shown in Figure 1. The gel time of the system containing 5 wt % AlBw whisker without treatment is almost same as that of BADCy/E-51 system. The gel time of the systems containing 5 wt % AlBw whisker treated with KH550 and BE4 at 140°C were 15 and 14 min, respectively, which were only 3 min and 4 min less than the ones of without whisker addition at the same temperature.

The DSC analysis of thermal copolymerization behavior of two kinds of systems at a scan rate of 10°C/min was investigated and the results are depicted in Figure 2. BADCy/E-51 system (A) has an onset of exothermic copolymerization temperature at ~ 183°C, with a processing window of 138–220°C. The DSC scans of curing process of BADCy/E-51/AlBw whisker system (B1) exhibit an exothermic peak from ~ 131 to 216°C, with the exothermic peak maximum shifting from to 195°C compared with system A. And the BADCy/E-51/AlBw whisker system containing 4 wt % of BE4 (E4) shifted the exothermic peak maximum further to 187°C.

By this token, the curing reaction activity of BADCy/E-51/AlBw whisker system is little higher than that of BADCy/E-51 system. The influence of whisker on reaction activity of resin system is because of coupling agent using surface treatment of whisker. The amidocyanogen (—NH_2) of coupling agent reacted with not only epoxy groups but also cyanate groups, and is catalyzer of the curing reaction. On the other hand, a little whisker content led to less coupling agent content. Therefore, the reaction activity of resin system is affected quite little by addition of whisker.

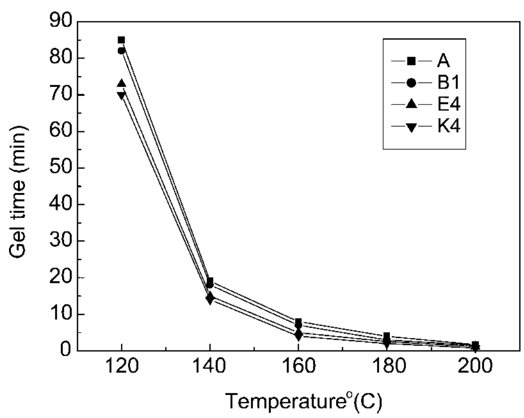

Figure 1 Gel time of BADCy/E-51 system and modified resin versus temperature.

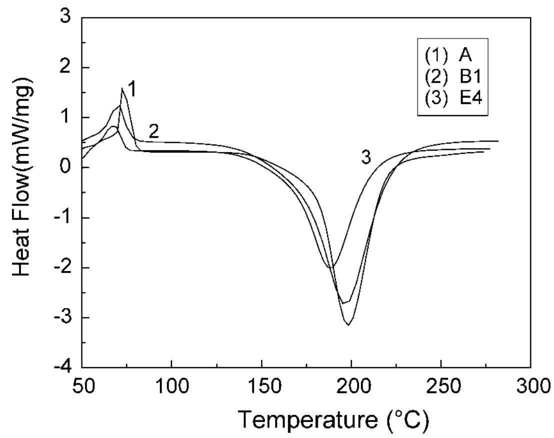

Figure 2 DSC curves of BADCy/E-51 system and modified resin system.

Mechanical properties of BADCy/E-51/ whisker system

The influence of coupling agent species and concentration on the impact strength of BADCy/E-51/AlBw system is shown in Figure 3. It is found that the addition of AlBw whisker without surface treatment cannot enhance toughness of BADCy/E-51 system. After treated by silane and borate ester, AlBw whisker can improve impact strength, and the effect of improvement of whisker treated by borate ester is more than whisker treated by silane. The impact strength of the systems will increase with the coupling agent content rising up to 4 wt %. When the content of coupling agent is higher than 4 wt %, the impact strength of system slightly decreases.

The interfaces between resin and whisker without surface treatment adhere poorly and are destroyed first when materials yield to impact. Therefore, the addition of AlBw whisker without surface treatment decreases toughness of system. The borate ester could combine with AlBw whisker because of the

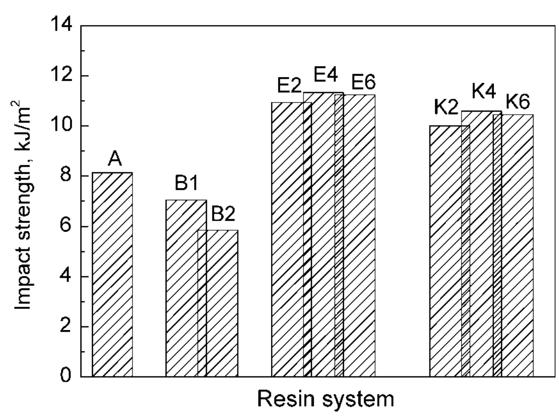

Figure 3 Influence of coupling agent on mechanical properties of resin system.

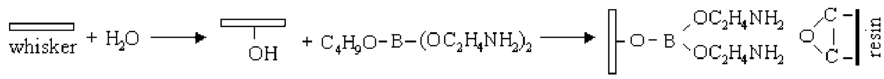

Figure 4 Possible reaction of BE4 with AlBw and resin.

physical sorption of central boron atom and AlBw whisker, the chemical reaction of butoxy on borate ester, and hydroxyl of AlBw whisker as well. The surface activity of whisker is enhanced by treatment by BE4. On the other hand, the amidocyanogen of BE4 could react with cyanate ester resin and epoxy resin. The reaction between AlBw whisker, resin, and BE4 is shown in Figure 4. Therefore, BE4 acts like a bridge to improve the connection of interface and enhance the toughness of materials.

The impact rupture SEM photos of system including 8 wt % AlBw whisker treated by silane and borate ester, respectively, are shown in Figure 5. The agglomeration phenomenon of whisker is found in system including AlBw whisker treated by KH550. However, there is not obvious agglomeration phenomenon found in system containing AlBw whisker treated by BE4. Consequently, the dispersion property of whisker is improved by adopting borate ester coupling agent to treat AlBw whisker. The rupture surface shape of system including whisker treated by BE4 is more complex than the one of system including whisker treated by KH550, and puts up typical toughness rupture.

Neat curing resin materials have many interior disfigurements such as cavity, impurity, and incomplete structure. However, whisker materials have quite short diameters and almost no disfigurement existing. Owing to its perfect crystal structure and high regular atom arrange, the strength of a whisker is extremely high and close to the binding force of adjacent atoms. The influence of the content of AlBw whisker treated by 4 wt % BE4 on mechanical properties of curing BADCy/E-51 resin system is investigated, and the result is depicted in Figure 6. The addition of AlBw whisker could enhance both impact strength and flexural strength of resin system. When the AlBw whisker content rises, the impact strength of BADCy/E-51/AlBw whisker system is increased, and the highest impact strength reached with the content of AlBw whisker attains 8 wt %. The impact strength of resin system is heightened from 8.14 to10.33 kJ/m^2 and is 30 wt % higher than the one of BADCy/E-51 resin system. When the content of AlBw whisker is higher than 8 wt %, the impact strength of system slightly decreases. The flexural strength of resin system is slightly improved. When the content of whisker is 8 wt %, the flexural strength of system is increased from 108 to 125 MPa.

There are three kinds of mechanism of whisker toughening resin materials, such as crack bridging, crack deflection, and pullout effect. Firstly, because of the existence of whisker, there are interface split areas between whisker and resin near top end of crack. In that area, whiskers connect the cracks like a bridge and add a closing stress on surface of crack to prevent crack to extend and toughen resin. Secondly, when cracks meet whiskers, cracks have to extend round whiskers due to high modulus of

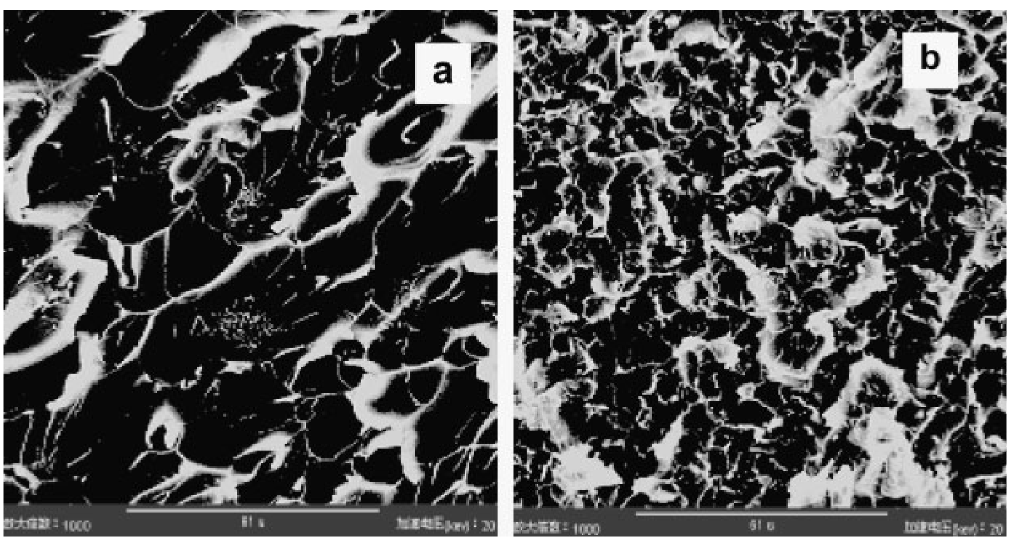

Figure 5 Fracture surface (×1000) of AlBw/BADCy/E-51 system treated by different coupling agent after impact [(a) treated by KH550; (b) treated by BE4].

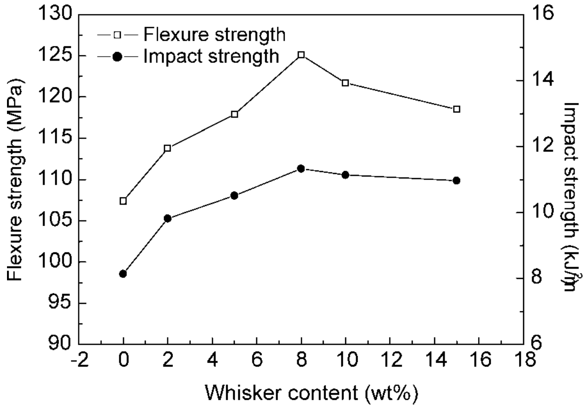

Figure 6 Influence of content of whisker on mechanical of modified resin system.

whisker. Crack deflection changes the route of crack extending, and crack plane is not upright to the axes of stress anymore. Accordingly, stress must increase to extend the crack. Moreover, there are areas of whisker pullout back of interface split areas. It is shown in Figure 7. When the materials rupture, the stress transferring from resin to whisker brings shear stress. The shear stress reaches the shear bend strength and whiskers are pulled out from resin, because whiskers possess high tensile strength unapt to rupture. The pullout of whisker consumes much energy to enhance the rupture strength.

The morphology of flexural fracture of BADCy/E-51/AlBw whisker system is analyzed by SEM. The photograph is shown in Figure 8. The whiskers pullout from resin and the micro-hole after drawing of whisker are found in the SEM photo. Thus it can be seen that the drawing effect exists in faith in BADCy/E-51/AlBw whisker system.

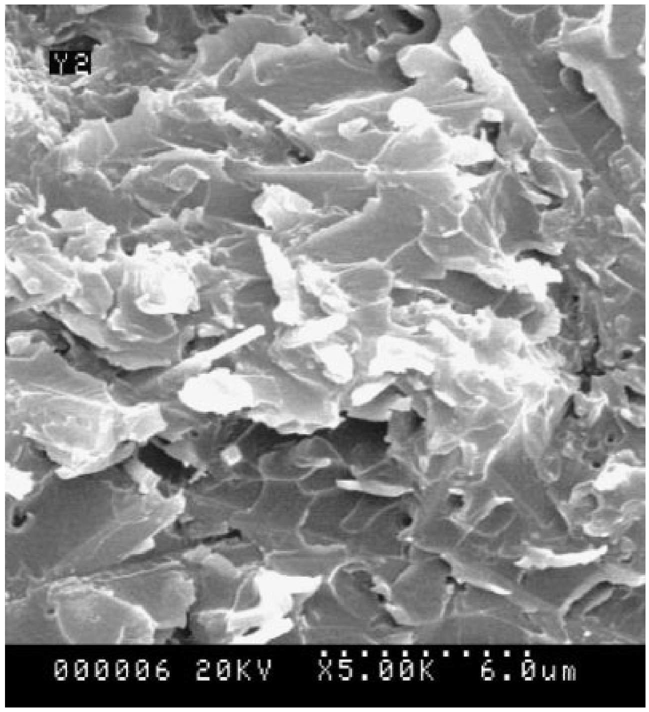

Figure 8 Fracture surface (×5000) of AlBw/BADCy/E-51 system.

Thermal properties of BADCy/E-51/AlBw system

Heat distortion temperature

The heat deflection temperature (HDT) of a material is an essential piece of information for product design. It represents the upper stability limit of the material in service without significant physical deformation (largely deflection) under load and thermal effect. HDT is defined as the temperature at which a specific deflection of a test bar (rests on two supports of a specified span) is obtained under a constant normal load.[14,15]

HDT values for cured BADCy/E-51/AlBw system were presented in Figure 9. The addition of AlBw without surface treatment decreases the HDT values of resin system with the increasing of AlBw content. This may be due to the interface between resin and whisker without surface treatment is not fast. HDT values of resin system included AlBw treated by BE4 and KH550 increase with the increase of AlBw content. This may be due to the rigid whisker

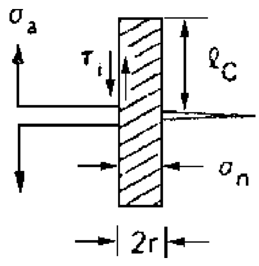

Figure 7 Sketch of drawing mechanism of whisker.

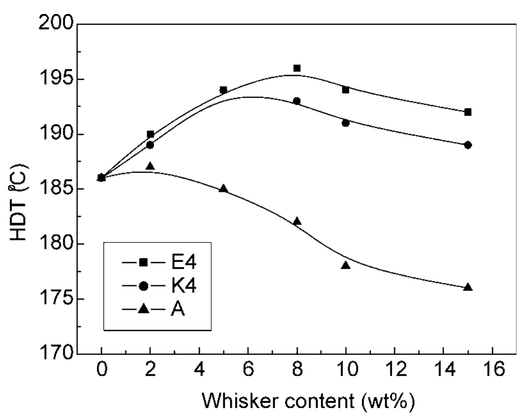

Figure 9 Influence of whisker content on HDT of resin system.

TABLE III
TGA Data of BADCy/E-51/AlBw System

System	T_i (°C)	Char yield at 700°C (%)
A	396	35.8
E4	418	38.6
E8	435	41.3
E10	428	44.7

restricted the molecules chain mobility. When the interface between resin and whisker is fast, there must be higher temperature to make the molecule chain movement and obtained a specific deflection of the material under a constant normal load, and as a result the higher HDT value. AlBw treated by BE4 integrates with resin more hard than the one treated by KH550. On the other hand, in resin system, AlBw treated by BE4 disperses better than the one treated by KH550. All of these factor would make HDT values of system included AlBw treated by BE4 higher than the one of system included AlBw treated by KH550.

Thermal stability

TGA curves of BADCy/E-51 system and BADCy/E-51/AlBw system included different content whisker treated by 4 wt % BE4. The decompose temperature (T_i) and the char residue (ΔW_r) obtained from the TGA curves could reflect the thermal stability of the cured hybrid resins.[16,17] Table III showed the T_i and the ΔW_r at 700°C values of different resin system.

The initial decompose temperature (T_i) was the temperature at which the weight loss is about 5%. The 5% mass loss temperatures for BADCy/E-51 and E4 were 396°C and 418°C, respectively. That is T_i increased 22°C when the addition of whisker is only 5 wt %. The T_i value for E8, attaining maximum, was 435°C, that is increased almost 40°C. However, the T_i value for E10, slightly decreased, was 428°C. Whisker is a kind of inorganic material that possesses excellent thermal stability. So the addition of whisker improves the thermal stability of resin system. However, when the content is more than 8 wt %, whisker could not disperse equably so as to tamper with improved effect.

The char residues (ΔW_r) were taken as the weight percentage of the sample remains after the TGA test, which for BADCy/E-51 resin system is 35.8% at 700°C. The char residues increased with whisker content increasing in resin system. While it increased from 38.6 to 44.7% as the whisker content increased from 5 to 10 wt %.

Hot–wet resistance of BADCy/E-51/whisker system

A resin with poor hot–wet resistance usually has high moisture absorption, causing a lowering of thermal stability and associated reliability problems. Therefore, hot–wet resistance is very important for developing a new resin.

The influence of AlBw whisker content on the hot–wet properties of BADCy/E-51 resin system is shown in Table IV. The whisker used for hot–wet resistance experiment is treated with 4 wt % content of BE4. The reason is that the best mechanical properties were obtained with this kind of whisker as discussed above and it is expected to achieve optimistic overall performance including hot–wet resistance, it is expected to achieve. The addition of whisker decreases the water absorption of resin system. After aging for 100 h in boiling distilled water, the water absorption of BADCy/E-51/AlBw whisker system including 8 wt % whisker is 1.92%, which is less almost 30% than the one of BADCy/E-51 resin system. When the whisker content is more than 8 wt %, the water absorption of BADCy/E-51/AlBw whisker system is slightly increased, because the amount of interface between resin and whisker is increased with increasing of whisker content. However, the water absorption is still less than the one of BADCy/E-51 resin system.

In the same way, when the whisker content is less than 8 wt %, the retention of mechanical strengths increases with increasing of whisker content. When the whisker content is 8 wt %, the retention of impact strength and flexural strength is 91 and 89%, respectively. When the whisker content is more than

TABLE IV
Influence of Whisker on Hot–Wet Properties of Modified Resin

Content of whisker (wt %)	Water absorption (%)	Impact strength (kJ/m^2)	Retention (%)	Flexure strength (MPa)	Retention (%)	HDT (°C)	
						Dry	After aging
0	2.67	7.50	83	87.0	81	186	172
2	2.35	9.03	86	96.7	85	190	179
5	2.01	9.25	88	105.4	89	194	180
8	1.92	10.20	90	111.3	89	196	181
10	2.07	9.69	87	106.9	88	195	178
15	2.24	9.43	86	100.7	87	196	176

8 wt %, the retentions of mechanical strengths decrease slightly with increasing of whisker content. The amount of interface between resin and whisker increases because of the increase of whisker content and the strength of some interfaces is not enough. By dipped in boiling water for a long time, rupture takes place in that weak interface firstly so as to decrease mechanical strength of system.

After aging for 100 h in boiling distilled water, the HDT values of BADCy/E-51/AlBw system is still higher than 175°C. Both of these changes are almost 90% retention of their original values, indicating that BADCy/E-51/AlBw whisker system has good hot–wet resistance.

CONCLUSION

Whisker treated with silane (KH550) and borate ester (BE4) coupling agents was used to modify cyanate ester/epoxy resin system. The impact strength of resin system was enhanced obviously without deceasing in flexural strength for the presence of treated whisker. The addition of whisker treated by coupling agent enhances reaction activity of BADCy/E-51 system slightly. The dispersibility of whisker in resin system could be improved by treating with BE4. SEM analysis shows that the toughening mechanism accords with pullout effect. Moreover, the thermal stability and hot–wet resistance of BADCy/E-51 system are improved by the addition of whisker.

References

1. Hamerton, I. Chemistry and Technology of Cyanate Ester Resins; Chapman and Hall: Glasgow, 1994; p 2.
2. Fang, T.; Shimp, D. A. Prog Polym Sci 1995, 20, 61.
3. Hamerton, I.; Barton, J. M.; Chaplin, A.; Howlin, B. J.; Shaw, S. J. Polymer 2001, 42, 2307.
4. Takao, I.; Takanori, M.; Masao, T. J Appl Polym Sci 1999, 74, 2931.
5. Hwang, J. W.; Park, S. D.; Cho, K.; Kim, J. K.; Park, C. E.; Oh, T. S. Polymer 1997, 38, 1835.
6. Borrajo, J.; Riccardi, C. C.; Williams, J. J.; Cao, Z. Q.; Pascault, J. P. Polymer 1995, 36, 3451.
7. Courtney, T. H. Mechanical Behavior of Materials; McGraw Hill: New York, 1990; p 83.
8. Tjong, S. C.; Meng, Y. Z. Polymer 1998, 39, 5461.
9. Demei, Y.; Jingshen, W.; Limin, Z.; Darong, X.; Songzheng, W. Compos Sci Technol 2000, 60, 499.
10. Tjong, S. C.; Meng, Y. Z. Polymer 1999, 40, 7275.
11. Zhimin, D.; Lizhen, F.; Shujin, Z.; Cewen, N. Mater Res Bull 2003, 38, 499.
12. Biaobing, W.; Zuowan, Z.; Lixia, G. Mater Res Bull 2003, 38, 1449.
13. Chazeau, L.; Cavaille, J. Y.; Terech, P. Polymer 1999, 40, 5333.
14. Vaia, R. A.; Price. G.; Ruth, P. N.; Nguyen, H. T.; Lichtenhan, J. Appl Clay Sci 1999, 15, 67.
15. Jarus, D.; Scheibelhoffer, A. Hiltner, A.; Baer, E. J Appl Polym Sci 1996, 60, 209.
16. Mantz, R. A.; Jones, P. F.; Chaffee, K. P. Lichtenhan, J. D, Gilman, J. W. Chem Mater 1996, 8, 1250.
17. Hsiue, G. H.; Liu, Y. L.; Wei, W. L.; Chen, W. Y. J Polym Sci Part A: Polym Chem 2003, 41, 432.