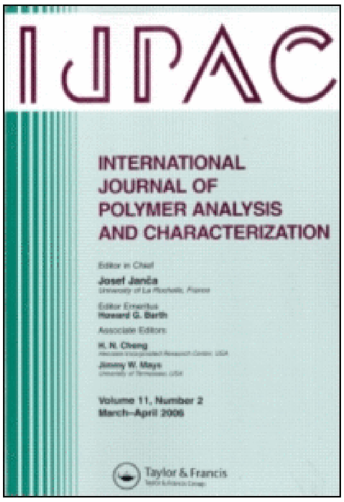

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Characterization of SiC Whisker-Filled Polybenzoxazine Cured by Microwave Radiation and Heat

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To cite this Article Rimdusit, S. , Jiraprawatthagool, V. , Tiptipakorn, S. , Covavisaruch, S. and Kitano, T.(2006) 'Characterization of SiC Whisker-Filled Polybenzoxazine Cured by Microwave Radiation and Heat', International Journal of Polymer Analysis and Characterization, 11: 6, 441 — 453

To link to this Article: DOI: 10.1080/10236660600983726

URL: http://dx.doi.org/10.1080/10236660600983726

International Journal of Polymer Anal. Charact., 11: 441–453, 2006
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ISSN: 1023-666X print
DOI: 10.1080/10236660600983726

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Abstract: The effect of microwave and thermal curing on the properties of SiC_W-filled polybenzoxazine is examined. The benzoxazine resin (BA-a) can be cured thermally above 150°C but was hardly cured by microwave irradiation even using a power up to 1 kW. The presence of only 4% by weight of the SiC_w significantly reduces the processing time of the composites from two hours at 200°C using the traditional thermal cure to less than 20 minutes using a microwave cure power of 270 W. The mechanical and thermal behaviors of the SiC_W-filled polybenzoxazine show no significant difference with either curing methods.

Keywords: Composite; Microwave processing; Polybenzoxazine; Silicon carbide whisker

Received 9 May 2006; accepted 28 August 2006.

This research was supported by the Rajchadapisek Fund of Chulalongkorn University of the year 2005. S.R. also gratefully acknowledges the additional financial support from the Research Grant for Mid-Career University Faculty of the Commission on Higher Education, Ministry of Education, and the Thailand Research Fund 2005–2007.

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INTRODUCTION

The application of microwaves was found to be an alternative method for curing thermosets with a significant increase in the rate of reaction.[1] In addition, the microwave-heated thermosetting composite was also shown to possess higher mechanical properties than those cured by conventional thermal process. This was believed to be due to the homogeneity heating that can reduce thermal stress in the composites.[2] In addition, microwave-cured epoxy composites were sometimes found to exhibit stronger interfacial bonding than that of thermal-cured systems.[3] However, microwave heating ability of any material depends significantly on its dielectric constants and dielectric loss factors.[4] Since most polymers possess a low dielectric constant,[5] microwave heating of neat polymers is not favorable. On the other hand, epoxy resins can be used in microwave heating because of the presence of some polar groups in their molecular structure. A significant increase in the rate of reaction was reported and an improvement in some mechanical properties was observed in an earlier study.[6] However, epoxy resins often provide a narrow processing window, have a short storage life, require a curing agent, and must be refrigerated for storage. Moreover, they are rather flammable and possess rather low thermal stability compared to phenolic resin.[7]

Polybenzoxazine is a novel class of phenolic resins that has been developed and studied to overcome the shortcomings of traditional phenolic resins.[8] Polybenzoxazine has the advantages of neither requiring any strong acids as catalysis nor producing any volatile by-product during polymerization. Its cross-linking reaction is achieved by a thermally activated ring-opening reaction.[9] Many attractive properties such as highly tailor-made molecular structure, low melt viscosity, self-polymerization upon heating, near zero shrinkage, high mechanical integrity, excellent electrical properties, high char yield, and ability to be alloyed with various types of existing polymers[10–12] have been reported for polybenzoxazine. However, like most polymeric materials, the low dielectric constant of polybenzoxazine means that it can not be cured conveniently by microwave radiation. Fortunately, the problem of the low dielectric constant of polymers can be improved by adding other suitable high dielectric constant filler.[13]

In order to enhance dielectric constant of material, Kitano et al.[14] reported the use of electro-conductive and inductive fillers such as short carbon fiber and silicon carbide whisker (SiC_w) for the heating or melt processing of polyethylene. The authors suggested that the major advantage of using SiC_w as a microwave-assisted coupling filler is due its effective heating and less sparking during irradiation compared to the use of short carbon fiber.[15] Moreover, SiC_w has been reported to exhibit outstanding toughening ability particularly with a rigid matrix such as found in many ceramics composite systems.[16] Therefore, it is anticipated that an incorporation of SiC_w into a polybenzoxazine matrix should render at least twofold benefits to the benzoxzine resin. The inherent rigidity of polybenzoxazine may be reduced by the toughening mechanisms occurring in the filled systems, while the high electric constant of the SiC_w should enhance the microwave curability of the filled polybenzoxazine.

EXPERIMENTAL SECTIONS

Materials

The materials in this research were benzoxazine resin and silicon carbide whisker. Benzoxazine resin is based on bisphenol-A, aniline, and formaldehyde. Bisphenol-A (commercial grade) was kindly supplied by Thai Polycarbonate Co., Ltd. (TPCC). Para-formaldehyde (AR grade) was purchased from Merck, and aniline (AR grade) was purchased from APS Finechem. Silicon carbide whisker was supplied by Tokay Carbon Co. All chemicals were used without further purification.

The benzoxazine resin used is based on bisphenol-A, aniline, and formaldehyde in the molar ratio of 1:4:2. This resin was synthesized by using a patented solventless method.[8] The obtained benzoxazine resin is a clear yellowish powder at room temperature and can be melted to yield a low viscosity resin at about 70°–80°C. The resin density is $1.2\,g/cm^3$ and it has a reported dielectric constant of about 3–3.5.[7] Silicon carbide whisker (SiC_w) used was TWS-200. It is a nearly perfect single crystal with an average diameter of $0.5\,\mu m$ and density of $3.2\,g/cm^3$. It has a reported dielectric constant of about 40.[17]

Specimen Preparation

Silicon carbide whisker was thoroughly mixed mechanically with benzoxazine resin in an aluminum container at 85°C for at least 10 min to ensure particle wet-out by the resin. The filler-to-matrix ratios were 0:100, 2:98, 4:96, and 6:94 by weight to yield molding compounds. For the thermal-cured specimen, the compounds were compression-molded to obtain a thickness of about 2 mm. The hot-pressed temperature of 200°C was applied for 2 h at a hydraulic pressure of 35 MPa. In the case of microwave curing, the molding compounds were cured in a microwave digestion oven (MARS5, model 907045) using a Teflon mold at a desired power from 100 to 1 kW and a fixed microwave frequency of 2.45 GHz.

Characterization Methods

The curing characteristics of the benzoxazine-silicon carbide composites were examined by using a differential scanning calorimeter (DSC) (TA, model 2910). For each test, a small amount of the sample ranging from 5 to 10 mg was placed on the aluminum pan and sealed in hermetically with aluminum lids. The experiment was done using a heating rate of 10°C/min to heat the sealed sample from 30° to 300°C under N_2 purging.

A universal testing machine (Instron, model 5567) was used to determine compressive properties under compression mode. The dimension of the specimen was 10 × 10 × 3 mm. The compression test was performed using a 1 kN load cell at a crosshead speed of 1 mm/min according to the procedure outlined in ASTM 695-02.

A dynamic mechanical analyzer (Netzsch, model DMA242) was employed to investigate the specimen's dynamic mechanical properties. The specimen dimension was 40 × 10 × 2 mm. The test was performed under bending mode. The strain was applied sinusoidally at a frequency of 1 Hz. The specimen was heated at the rate of 2°C/min from room temperature to 270°C. The dynamic storage modulus (E') was determined.

Observation of the interfacial bonding within the composites was investigated using a scanning electron microscope (SEM) (JEOL JSM-6400) at an acceleration voltage of 15 kV. All samples were coated with a thin film of gold using a JEOL ion sputtering device (model JFC-1100E) for 4 min to obtain a thickness of approximately 300 Å before micrographs of the magnified fracture surfaces of the composite were taken.

RESULTS AND DISCUSSION

Figure 1 demonstrates the DSC thermograms with the temperature elevating from 30° to 300°C, showing the influence of benzoxazine resin filled with different SiC_w contents on curing temperature. The step change at about 45°C observed in all thermograms with different SiC_w contents was related to the glass transition temperature of the benzoxazine resin. It is related to the liquefying point of this resin. Polymerization of benzoxazine resin was known to occur by a simple ring-opening addition reaction and does not yield any reaction by-products.[9] The curing exotherm of the benzoxazine molding compound at different SiC_w contents, shows the onset of cure at approximately 150°C. A maximum exotherm peak was observed at 225°C, which is the characteristic of this resin.[18] The silicon carbide whisker has no direct effect on chemical reaction during the curing process of the benzoxazine resins. This is because there is no observable peak shift in the thermograms and the reaction

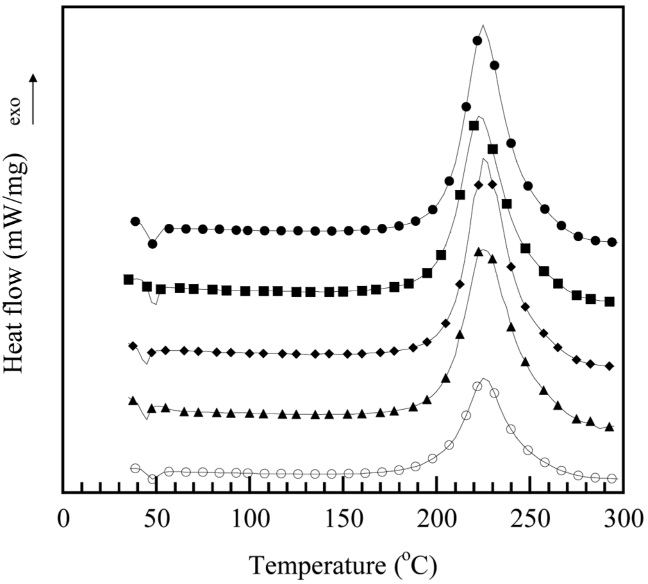

Figure 1. DSC thermograms of benzoxazine molding compound at various SiC_w contents: (●) 0, (■) 2, (◆) 4, (▲) 6, and (○) 20 wt.%.

temperature of SiC ceramics is above 1000°C.[19,20] However, the area under the curing peak was found to decrease with increasing SiC_w content.

Figure 2 demonstrates the effect of microwave heating on benzoxazine resin. The DSC thermogram of benzoxazine resin heated by a microwave at a high power of 1 kW for 30 min shows that under such condition, it was hardly cured; the change of the degree of conversion at this microwave irradiation condition was almost negligible. This is due to the intrinsic nonpolar nature of the benzoxazine resin.[8] However, with the addition of a relatively low content of SiC_w in the range of 4% by weight, the benzoxazine resin was found to be cured relatively well. This is evident in the DSC thermograms shown in Figure 3, when SiC_w of 4% by weight was used. Moreover, the input power needed to heat the SiC_w-filled benzoxazine resin to its full cure can be reduced substantially from over 1 kW to only 270–330 W. Hence it is apparent that the presence of SiC_w has a dramatic effect on curing of the benzoxazine molding compound. It was also found that higher microwave input power or longer irradiating time was needed as the SiC_w content decreased. With SiC_w loading of 4% by weight, the microwave radiation power of 270 W for 20 minutes was found to be the most suitable for processing of the benzoxazine molding compound to yield its fully cured state.

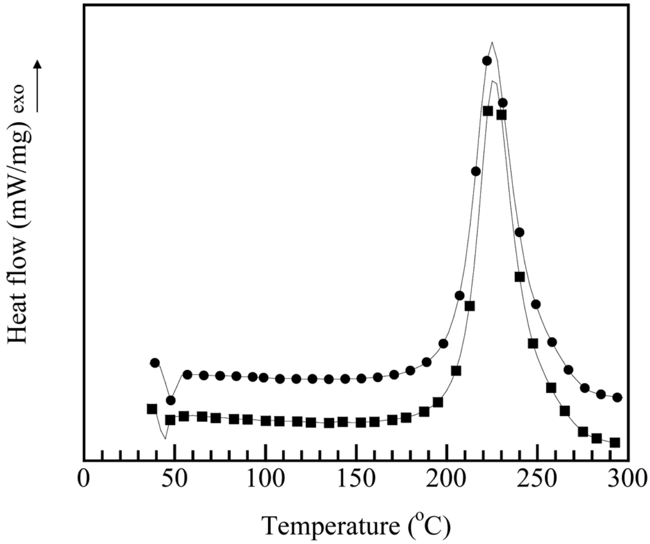

Figure 2. DSC thermograms of benzoxazine resin: (●) BA-a monomer, (■) BA-a monomer after irradiating with microwave power of 1 kW for 15 min.

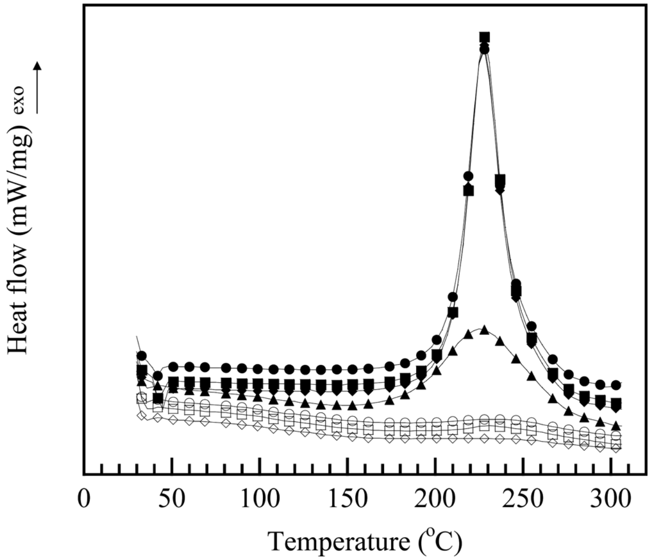

Figure 3. DSC thermograms of microwave-treated 4 wt.% SiC_w-filled polybenzoxazine molding compounds at fixed irradiation time of 15 min: (●) 150, (■) 180, (◆) 210, (▲) 240, (○) 270, (□) 300, and (◇) 330 W.

The conversion-time diagram of the microwave-cured benzoxazine resin filled with 4% by weight of SiC_w at 270 W is compared with that of the regular thermal cure in an oven heating at 200°C in Figure 4. The benefit of using the microwave technique is evidently depicted in the rapid rise of conversion in the microwave-cured compound. As shown in the diagram, curing time of only 20 minutes was required to convert the benzoxazine molding compound to its maximum cure by microwave processing at 2.45 GHz and 270 W, while the traditional oven cure at 200°C required at least 120 minutes.

Figure 5 shows the DSC thermograms depicting the glass-transition temperature (T_g), which was assigned as the midpoint temperature of the heat flow curve[21] of the neat benzoxazine resin and of the SiC_w-filled polybenzoxazine at 2, 4, and 6% by weight of the filler. At a heating rate of 10°C/min, the T_g of the polybenzoxazine was found to be 153°C. The T_g of all the SiC_w-filled polybenzoxazine composites cured thermally show no significant change from that of the neat polybenzoxazine, i.e., ranging from 153° to 160°C. The SiC_w filler was found to elevate the T_g of the composites due to the reinforcing effect of the ceramic filler to the matrix polymer. Boey and Yap[22] reported the maximum T_g of microwave-cured epoxy-amine system to be significantly lower than those achieved by thermal curing, because the sluggish reaction with microwave curing of the epoxy-amine system could entrap the functional group in the cross-link network. The different heating mechanisms, i.e., by

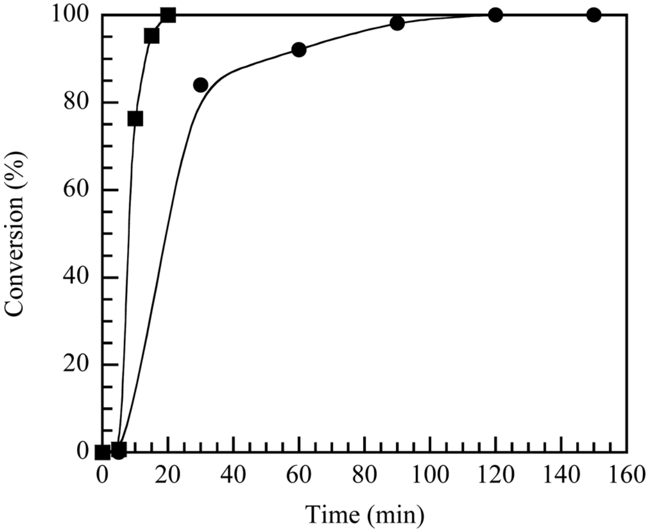

Figure 4. Conversion-time curve of 4 wt.% SiC_w-filled polybenzoxazine composite: (■) microwave-cured at 2.45 GHz, 270 W, (●) thermal-cured at 200°C.

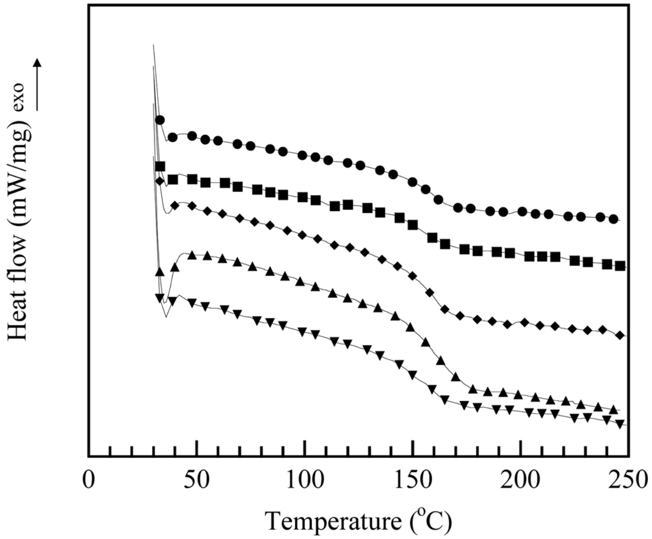

Figure 5. DSC thermograms of fully cured polybenzoxazine composites: (●) heat-cured polybenzoxazine, (□) heat-cured 2 wt% SiC_w, (◆) heat-cured 4 wt.% SiC_w, (▲) heat-cured 6 wt.% SiC_w, (▼) microwave-cured 4 wt.% SiC_w.

conduction of heat throughout the whole compound in the oven-cured technique and sporadic heating from the surface of the tiny silicon carbide whisker as well as the inside-out heating mechanism of the microwave during processing, may be the reasons for the discrepancy in T_g in some epoxy systems as mentioned above. In our case, at 4% by weight of SiC_w content, the microwave-cured SiC_w-filled polybenzoxazine composites possess a T_g of approximately 155°C, which is close to that of the heat-cured composites. The observed similar values of T_g implied no significant change in the curing mechanisms as well as no degradation of our benzoxazine resin upon microwave cure and heat-cure methods. This behavior had also been reported for some resin systems.[3]

Microwave radiation is believed to heat the whole composite simultaneously. In reality, since polymerization took place only within the resin and the reaction is exothermic, the temperature of the surrounding and the mold was always lower than that within the microwave-heated resin. Therefore, a temperature gradient may still exist due to heat conduction from the hot benzoxazine molding compound to the colder surrounding. For this reason, the percent conversion at different locations of the microwave-cured composite was investigated. The results are illustrated in Table I. It is evident that a relatively uniform curing of over 97% conversion was achieved at all locations in our fully cured composite. The maximum cure conversion of nearly 100% was detected at

Table I. Conversion at different positions of 4% by weight SiC_w-filled polybenzoxazine composite cured by microwave irradiation

Distance from center (cm)	Conversion (%)
–2	98.8
–1	98.3
0	100.0
1	98.5
2	97.7

the center of the composite sample. This test verified the uniformity of cure achieved in the microwave-cured polybenzoxazine/SiC_w composites prepared for further property characterization in our study.

Figure 6 exhibits the dynamic flexural moduli of the SiC_w-filled polybenzoxazine composites cured by traditional thermal heating with SiC_w contents ranging from 0 to 6% by weight and microwave heating with constant 4% by weight of SiC_w, the optimal content for microwave processing, with the temperature ranging from 30° to 260°C based on a heating rate of 2°C/min. The storage modulus of SiC_w-filled polybenzoxazine at its glassy state tends to increase with increasing SiC_w fraction in the

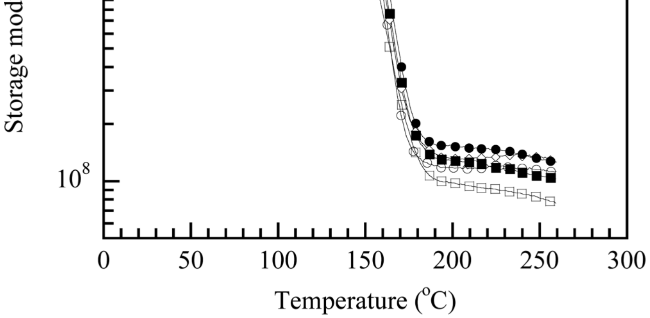

Figure 6. Storage modulus of fully-cured polybenzoxazine composites: (○) heat-cured polybenzoxazine, (□) heat-cured 2 wt.% SiC_w, (◇) heat-cured 4 wt.% SiC_w, (•) heat-cured 6 wt.% SiC_w, (■) microwave-cured 4 wt.% SiC_w.

composites as a result of the reinforcing effect of the more rigid SiC_w filler. At room temperature, the dynamic modulus of SiC_w-filled polybenzoxazine composite increased from 5.5 GPa of a neat polybenzoxazine to 6.2 GPa of the 6% by weight of SiC_w composite. The modulus of the SiC_w-filled polybenzoxazine in the rubbery plateau region was also enhanced by increasing SiC_w content, because the load transfer in the composite occurred mainly through the SiC_w, when the two phases contact. Therefore, the mobility and the deformability of the rubbery matrix could be reduced by the presence of the hard SiC_w. Since there was only a small amount of SiC_w content in the composite, the dynamic mechanical properties showed only marginal increase in values.

The stress-strain relation under axial compression of the polybenzoxazine composites is shown in Figure 7. Apparently, compression load increases with displacement until it reaches the intrinsic yield point of the specimens, and then it drops gradually despite increasing the displacement until composite failure. Strain softening, which was lacking in neat polybenzoxazine, was observed in all SiC_w-filled polybenzoxazine composites. The specific energy absorption (SEA) for the axial compression can be calculated by integrating the area under the load-displacement curves and dividing by the mass of the specimen.[23] From the experiment, the SEAs were found to increase with increasing the SiC_w content from

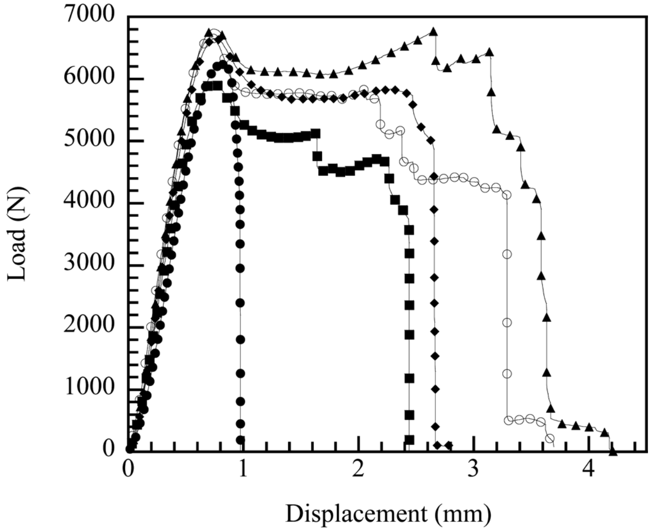

Figure 7. Load-displacement curve under axial compression of polybenzoxazine composites: (●) neat polybenzoxazine, (■) 2 wt.% SiC_w-filled PBZ cured by heat, (◆) 4 wt.% SiC_w-filled PBZ cured by heat, (▲) 6 wt.% SiC_w-filled PBZ cured by heat, (○) 4 wt.% SiC_w-filled PBZ cured by microwave.

the value of 25 kJ/kg of the unfilled polybenzoxazine, 36 kJ/kg for 4% by weight of SiC_w, to 49 kJ/kg of the 6% by weight of SiC_w-filled polybenzoxazine. The result suggested the promotion of energy absorption by the incorporation of SiC_w into the polybenzoxazine matrix. However, at a fixed 4% by weight of SiC_w-filled polybenzoxazine composite, the SEAs of the composites cured by both methods were approximately the same within the range of 31–42 kJ/kg for thermal-cured composites and 32–44 kJ/kg for microwave-cured composites. Both curing methods, therefore, showed negligible effect on changing the mechanical properties of the polybenzoxazine composites.

Figure 8 shows the interfacial characteristics along the fracture surface of the silicon carbide whisker-filled polybenzoxazine (at 2 and 4% by weight of filler) cured by hot-pressing and microwave radiation. The fracture surface of the neat polybenzoxazine is much smoother than that of the SiC_w-filled polybenzoxazine composite. Protruding whiskers and holes, where the whiskers were initially lodged before fracture, were also observed. There were also evidence of whisker pullout and bridging. This fracture characteristic might explain the enhancement of the SEAs of our polybenzoxazine matrix with the addition of the SiC_w, as discussed in the previous section. Moreover, the interfaces between the matrix and the SiC_w filler in the composite cured by microwave radiation revealed the same feature as that observed in the thermally cured composites. The result confirmed

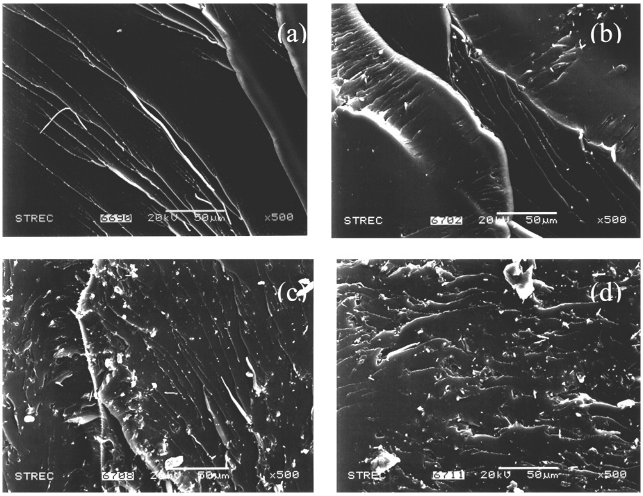

Figure 8. SEM micrographs of fracture surface of SiC_w-filled polybenzoxazine composites: (a) neat PBZ cured by heat, (b) 2 wt.% SiC_w-filled PBZ cured by heat, (c) 4 wt.% SiC_w-filled PBZ cured by heat, (d) 4 wt.% SiC_w-filled PBZ cured by microwave.

the observed similarity in the mechanical properties of our polybenzoxazine composites processed by both microwave and heat.

CONCLUSIONS

The effect of microwave cure and conventional thermal cure on thermal and mechanical properties of SiC_w-filled polybenzoxazine was investigated. The optimal SiC_w content to effectively couple with microwave to yield a fully cured polybenzoxazine was found to be about 4% by weight. The optimum processing condition of SiC_w-filled polybenzoxazine composites for thermal curing was 200°C for two hours, and for microwave curing it was 270 W for 20 minutes. The glass transition temperature and flexural modulus of the composites increased slightly within the evaluated SiC_w content up to 6% by weight and were not significantly affected by the two processing methods. The specific energy absorption upon uniaxial compression was found to increase with the SiC_w content. The SEM micrographs of the composite fracture surfaces revealed substantial adhesion between the SiC_w and the polybenzoxazine matrix.

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