

# Comparison of Microwave and Thermal Cure of Epoxy-Anhydride Resins: Mechanical Properties and Dynamic Characteristics

Varaporn Tanrattanakul,<sup>1</sup> Kaew SaeTiaw<sup>2,\*</sup>

<sup>1</sup>Polymer Science Program, Faculty of Science, Prince of Songkla University, Hatyai, Songkla, 90112 Thailand

<sup>2</sup>Materials Engineering Program, Faculty of Engineering, Prince of Songkla University, Hatyai, Songkla, 90112 Thailand

Received 21 September 2004; accepted 16 November 2004

DOI 10.1002/app.21578

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The objective of this work was to compare the mechanical properties of epoxy resins cured by thermal heating and microwave heating. Epoxy-anhydride (100:80) resins were cured in a domestic microwave oven and in a thermal oven. The hardening agents included methyl tetrahydrophthalic anhydride and methyl hexahydrophthalic anhydride. Three types of accelerators were employed. Thermal curing was performed at 150°C for 20 and 14 min for resins containing 1 and 4% accelerator, respectively. Microwave curing was carried out at a low power (207 or 276 W) for 10, 14, and 20 min. All cured resins were investigated with respect to their tensile properties, notched Izod impact resistance, and flexural properties (three-point bending) according to ASTM standards. The  $\tan \delta$  and activation energy values were investigated with dynamic mechanical thermal analysis, and the extent of conversion was determined with

differential scanning calorimetry. The differences in the mechanical properties of the thermally cured and microwave-cured samples depended on the resin formulation and properties. Equivalent or better mechanical properties were obtained by microwave curing, in comparison with those obtained by thermal curing. Microwave curing also provided a shorter cure time and an equivalent degree of conversion. The glass-transition temperatures ( $\tan \delta$ ) of the thermally and microwave-cured resins were comparable, and their activation energies were in the range of 327–521 kJ/mol. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1442–1461, 2005

**Key words:** activation energy; composites; crosslinking; curing of polymers; resins

## INTRODUCTION

The utilization of microwaves for heating began in the 1940s. Studies of the microwave processing of polymers in the early 1960s led to several successful applications in the rubber, textile, and food industries. Since the mid-1980s, there has been a great deal of interest in the microwave processing of polymers.<sup>1–35</sup> Because the mechanism of microwave heating is independent of thermal conductivity, microwave heating avoids heat-transfer-rate problems encountered in conventional thermal heating, for which the low thermal conductivity of polymers is problematic. This relatively new form of energy transfer offers many distinct advantages over conventional heating, such as volumetric, fast, directly selective, instantaneous, and

controllable heating. Microwave energy, with its long wavelength, offers deeper penetration than ultraviolet or electron-beam irradiation but does not possess sufficient energy to cause bond cleavage. Only accelerated dissipative heating occurs in microwave processing. In this way, energy may be distributed rapidly throughout the volume of a material. Surface overheating or uneven accelerator decomposition is avoided.

In conventional thermal processing, energy is transferred to the material through the convection, conduction, and radiation of heat from the surfaces of the material. In contrast, microwave energy is delivered directly to materials through molecular interactions with the electromagnetic field. This results in rapid heating throughout the material's thickness with reduced thermal gradients. Volumetric heating can also reduce the processing time and save energy. The ability to process polymeric materials with microwaves depends on the applied frequency, electric field strength, dipole structure, additives or fillers that have been included with the polymer, and dielectric properties of the polymer. When two materials are simultaneously subjected to microwave irradiation, the

Correspondence to: V. Tanrattanakul (varaporn.t@psu.ac.th).

\*Present address: Thai Composites Company, Limited, Bangkok, Thailand.

Contract grant sponsor: Thailand Research Fund; contract grant number: RSA4580041.

TABLE I  
Characteristics of the Chemicals

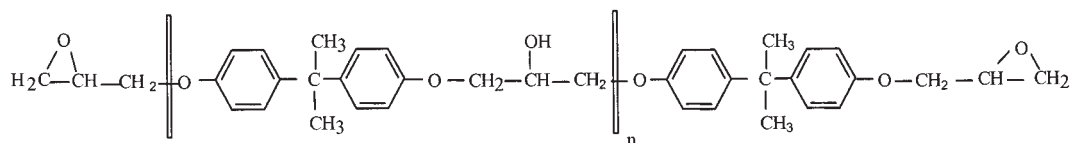
| Chemical | Grade                | Viscosity at 25° (cP) | EEW | AE  | Supplier                                |
|----------|----------------------|-----------------------|-----|-----|---|
| Epoxy    | DER 331 <sup>a</sup> | 11,800                | 189 | —   | Dow Chemical Co. (Midland, MI)          |
| MTHPA1   | Lindried® 46QC       | 60                    | —   | 166 | Lindau Chemicals Co. (Columbia, SC)     |
| MTHPA2   | EG/NT                | 50                    | —   | 166 | LonzaSpa Co. (Milan, Italy)             |
| MHHPA    | SW                   | 53                    | —   | 168 | LonzaSpa Co. (Milan, Italy)             |
| DMP-30   | Ancamine K54         | 200                   | —   | —   | Anchor Chemical, Ltd. (Los Angeles, CA) |
| EMI      | Imicure EMI24        | 6,500                 | —   | —   | Air Products and Chemicals, Inc.        |
| BDMA     | Purum (>98%)         | —                     | —   | —   | Fluka (Buchs, Switzerland)              |

EEW = epoxy equivalent weight; AE = anhydride equivalent.

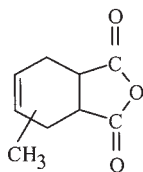
<sup>a</sup>  $n = 0.15$ .

higher dielectric loss material is heated more rapidly than the lower dielectric loss material. With microwave irradiation as a heating source, chemical reactions occur. This leads to the study of microwave-

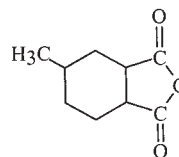
induced chemical reactions. A controversial topic in this study is whether there is a microwave effect, or nonthermal effect, on chemical reactions beyond heating. On the basis of the research published so far, there



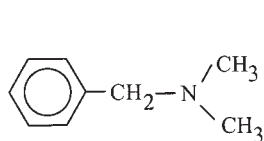
DGEBA,  $n = 0.15$



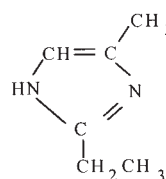
MTHPA



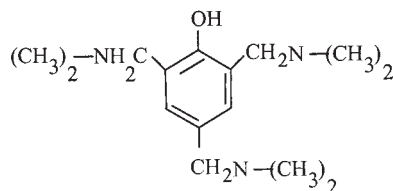
MHHPA



BDMA



EMI



DMP-30

Figure 1 Chemical structures of the epoxy (DGEBA), hardeners (MTHPA and MHHPA), and accelerators (BDMA, EMI, and DMP-30).

TABLE II  
Sample Designation and Composition

| Resin | Hardener | Accelerator |
|-------|----------|-------------|
| I     | MTHPA1   | Unknown     |
| II    | MHHPA    | DMP-30      |
| III   | MHHPA    | EMI         |
| IV    | MHHPA    | BDMA        |
| VI    | MTHAP2   | DMP-30      |
| VII   | MTHPA2   | EMI         |
| VIII  | MTHPA2   | BDMA        |

is still no consensus.<sup>9,17,19</sup> Critics of the microwave effect often claim that differences can be attributed to poor temperature measurement and control of experimental conditions that result in systematic error. The existence or nonexistence of a microwave effect continues to be an area of considerable debate and research.

Epoxy resins are among the most important thermosets and have many major industrial applications, such as surface coatings, adhesives, and fiber-reinforced composites. Major barriers to the use of thermosetting composites in many applications include the long cure and postcure processing times required to achieve the required mechanical properties. There has been much research in the area of microwave processing for epoxy resins, including epoxy-amine systems<sup>4-12,15-24,27,28</sup> and epoxy-anhydride systems.<sup>26,33</sup> Some research groups have employed domestic microwave ovens without modification,<sup>9,14,35</sup> and others have modified domestic microwave ovens with a magnetic stirrer<sup>9</sup> or to accommodate a fiber-optic probe,<sup>34</sup> but some of them have not provided details of the modification.<sup>15</sup> Therefore, a domestic microwave oven is applicable to scientific experimentation. Galema<sup>32</sup> also mentioned the application of a domestic microwave oven. Most researchers have studied the kinetics or chemical reactions (extent of curing) and physical properties, that is, the glass-transition temperature ( $T_g$ ) and dielectric properties. A few publications report the mechanical properties of microwave-cured epoxy.<sup>7,9,11,26</sup> There is controversy over the kinetics of curing and mechanical properties of microwave-cured samples in comparison with those of thermally cured samples. The reaction rate, cure time, and  $T_g$  of microwave-cured epoxy have been reported to be dependent on the resin system (hardener/curing agents).<sup>4,20,21</sup> No microwave effect on the kinetics of epoxy curing and the three-dimensional structure has been proposed,<sup>15,28</sup> but some researchers have proposed rate enhancement by microwave curing.<sup>9,18,27</sup> Small changes in the mechanical properties of microwave-cured epoxy have been reported,<sup>7,11</sup> whereas increases and decreases in the tensile properties have been observed.<sup>9</sup> Disagreements on the properties of microwave-cured samples may result from the following factors:

- The resin system: Different chemicals show different dipole structures and dielectric properties, and these result in different behaviors.
- The microwave oven: Different cavities (including the cavity shape and cavity material) and different modes affect microwave power dissipation. The irradiation of a pulsed-power microwave oven differs from that of a continuous-power microwave oven.<sup>19</sup> The uniformity of the electric field and position of the sample are also important. Nonuniformity within the electromagnetic field will result in nonuniform heating.
- The sizes and shapes of the samples: The temperature at the center of a sample is higher than that at the sample's boundaries because of the slow heat conduction inside the sample. An increase in the curing time allows heat transfer from the center to the boundaries, and this leads to more homogeneity.<sup>7</sup>
- The curing conditions: The microwave power and curing time control the temperature of a sample.

In this work, we report the results of a systematic study of epoxy-anhydride resins cured in a home microwave oven. Because multimode systems are the most common processing systems used in industrial applications<sup>17</sup> and this research involves industrial work, we used a domestic microwave oven. Data obtained from this work will be applied to industrial work in the future. The mechanical properties and dynamic mechanical thermal analysis (DMTA) of the microwave-cured epoxy resins are compared with those of conventional thermally cured resins. To the best of our knowledge, our resin systems have not yet been reported in the microwave-curing literature. Because this work is focused on the efficiency of microwave curing and the mechanical properties of the selected epoxy system, direct comparisons between the kinetics of curing activated by thermal and microwave heating are beyond the scope of this study, and the kinetic mechanisms during the polymerization of the reactive system are not the aim of this article. The mechanisms of the epoxy-anhydride system are very complex, and for that reason, many works in the references do not include the mechanisms of curing reactions. However, the mechanisms of the epoxy-anhydride reaction are reported in many publications.<sup>36-39</sup>

TABLE III  
Heating Conditions

| Source of heat | Accelerator (%) | Condition          |
|----------------|-----------------|--------------------|
| Oven           | 1               | 150°C, 20 min      |
|                | 4               | 150°C, 14 min      |
| Microwave      | 1               | 10 and 14 min      |
|                | 4               | 10, 14, and 20 min |

TABLE IV  
Calibration Data of Microwave Power

| Level | Setting power (W) <sup>a</sup> | Magnetron's output power (W) <sup>b</sup> | Equivalent power (W) <sup>c</sup> |
|-------|--------------------------------|---|-----------------------------------|
| 1     | 80                             | —   | —                                 |
| 2     | 160                            | 71  | 138                               |
| 3     | 240                            | 158                                       | 207                               |
| 4     | 320                            | 249                                       | 276                               |
| 5     | 400                            | 352                                       | 345                               |
| 6     | 480                            | 406                                       | 414                               |
| 7     | 560                            | 513                                       | 483                               |
| 8     | 640                            | 586                                       | 552                               |
| 9     | 720                            | 610                                       | 621                               |
| 10    | 800                            | 698                                       | 690                               |

<sup>a</sup> Data derived from the producer.

<sup>b</sup> Experimental data derived from measurements based on ref. 29.

<sup>c</sup> Data derived from a linear regression with  $R^2 = 0.9732$ .

## EXPERIMENTAL

### Materials

The chemicals are listed in Table I. The epoxy resin was a general-purpose-grade diglycidyl ether of bisphenol A (DGEBA) with  $n = 0.15$ . Two hardeners were employed: methyl tetrahydrophthalic anhydride (MTHPA) and methyl hexahydrophthalic anhydride (MHHPA). The accelerators included tris-2,4,6-dimethyl aminomethyl phenol (DMP-30), 2-ethyl-4-methyl imidazole (EMI), and *N*-benzyl dimethylamine (BDMA). MTHPA1 contained an unknown accelerator, whereas MTHPA2 and MHHPA contained no accelerator. The chemical structures of all the materials are shown in Figure 1. All the chemicals were commercial-grade and were used as received.

### Sample preparation

The main suppliers of the anhydride hardeners suggested using approximately 80–90 wt % of the anhy-

TABLE V  
Comparison of the Setting Time and Heating Time of the Microwave Oven

| Level          | Equivalent power (W) <sup>a</sup> | Setting time (min) | Actual heating time (min) |
|----------------|-----------------------------------|--------------------|---------------------------|
| 3 <sup>b</sup> | 207                               | 10                 | 3                         |
|                |                                   | 14                 | 4                         |
|                |                                   | 20                 | 6                         |
| 4 <sup>b</sup> | 276                               | 10                 | 4                         |
|                |                                   | 14                 | 6                         |
|                |                                   | 20                 | 8                         |

<sup>a</sup> Data from TABLE IV.

<sup>b</sup> Refers to 30 and 40% of 800 W, respectively (= 240 and 320 W of setting power, respectively), according to the product data sheet.

drude/epoxy stoichiometric ratio to obtain better properties. For that reason, we employed a ratio of 80:100 anhydride/epoxy. The concentration of the accelerator was 1 or 4 parts per hundred parts of epoxy resin. The sample designations and compositions are listed in Table II. After good mixing, air bubbles were released from the resin before it was poured into a mold. A chromium-coated steel plate was used as a mold for thermal curing, whereas a Teflon mold (17 cm in diameter and 3 cm deep) was used for microwave curing. The amount of the resin was weighed to control the thickness of the specimens. A Memmert U500 oven (Schwabach, Germany) was employed for thermal curing. Microwave curing was performed in a Sanyo EM-X412 commercial microwave oven (Sanyo Thailand Co., Bangkok, Thailand) at a frequency of 2.45 GHz. This microwave oven was fitted with a voltage controller to facilitate the processing power (to be specified). It consisted of 10 power levels, with the maximum level equal to 800 W. In this work, the applied power was based on the physical performance of the cured samples. No air bubbles and no burning

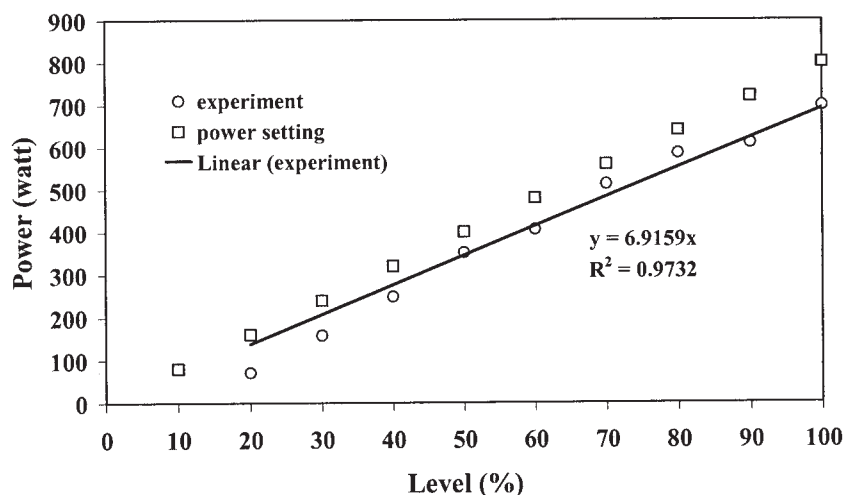
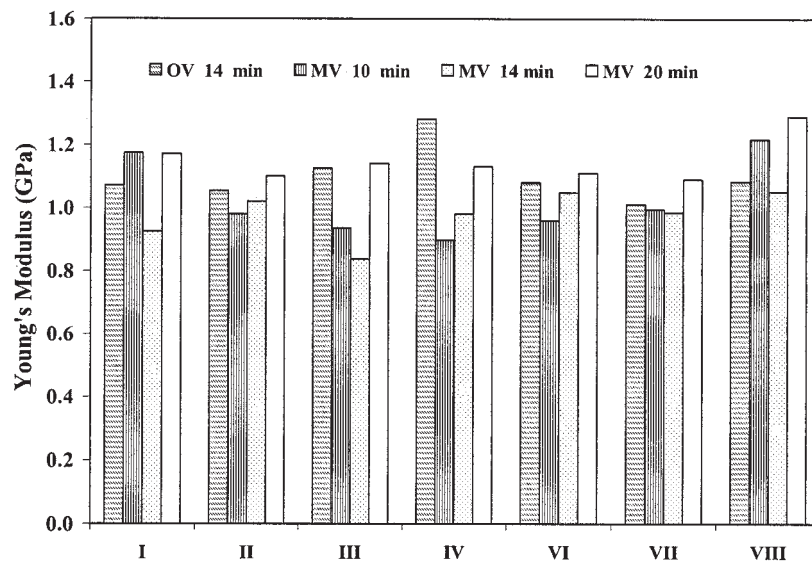
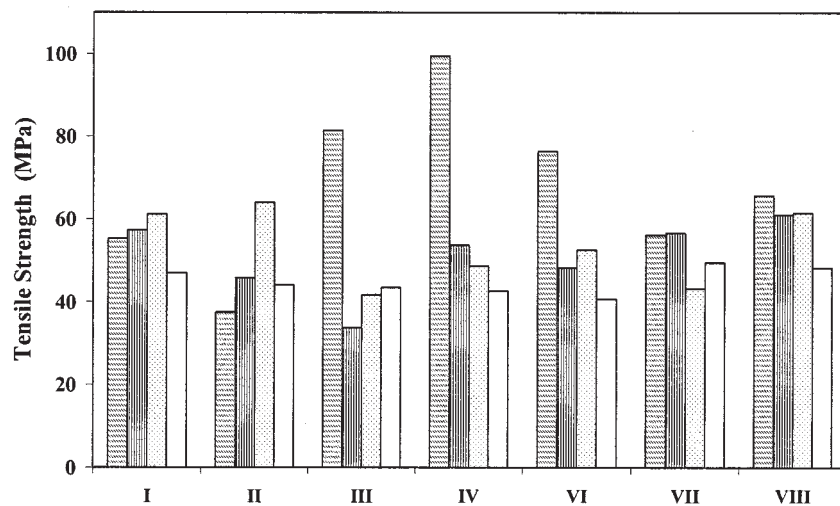


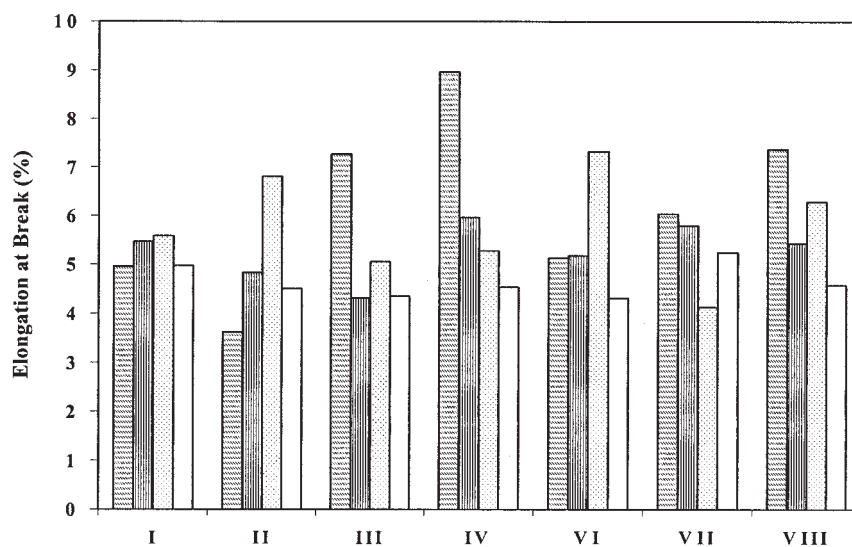
Figure 2 Calibration curve of the microwave output.



(a)

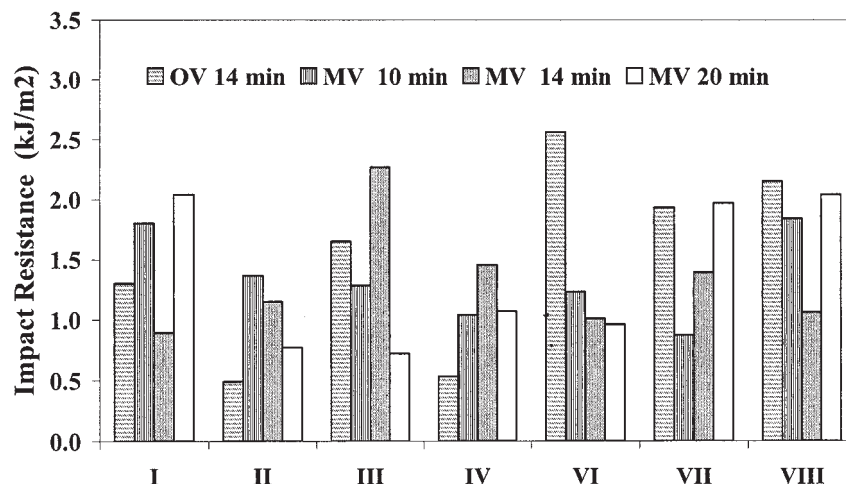


(b)



(c)

**Figure 3** Tensile properties of the epoxy resins containing 4% accelerator (OV = oven cure, MV = microwave cure): (a) Young's modulus, (b) tensile strength, and (c) elongation at break. The accelerator concentration of resin I was unknown.



**Figure 4** Impact strength of the epoxy resins containing 4% accelerator (OV = oven cure, MV = microwave cure). The accelerator concentration of resin I was unknown.

were criteria for good specimens. The optimal power level of resins I, II, VI, and VIII was the fourth level (power setting = 320 W), whereas resins III, IV, and VII were cured at the third level (power setting = 240 W). The heating conditions for microwave curing and thermal curing are described in Table III.

### Mechanical property testing

The tensile properties, flexural properties (three-point bending), and notched Izod impact resistance were tested according to ASTM D 638 (type I), ASTM D 790, and ASTM D 256, respectively. The tensile testing was conducted at a tension speed of 5 mm/min and at a gauge length of 50 mm. The three-point-bending test was executed at a speed of 8 mm/min with a span width of 25 mm; the specimen dimensions were 25 × 50 mm<sup>2</sup>. The specimen thickness was approximately 1.5 mm. Five specimens or more were tested for every sample for all the testing.

### Differential scanning calorimetry (DSC) analysis

The extent of conversion ( $\chi$ ) of the cured samples was determined with a PerkinElmer DSC7 (Norwalk, CT) at a heating rate of 20°C/min from 30 to 250°C. The heat of the complete reaction was obtained through the curing of fresh resins under the DSC heating scan. The area under the exothermic peak represented the heat of reaction. The specimens were cut from the area near the center of the cured samples or along the gauge length of the tensile specimens.

### DMTA

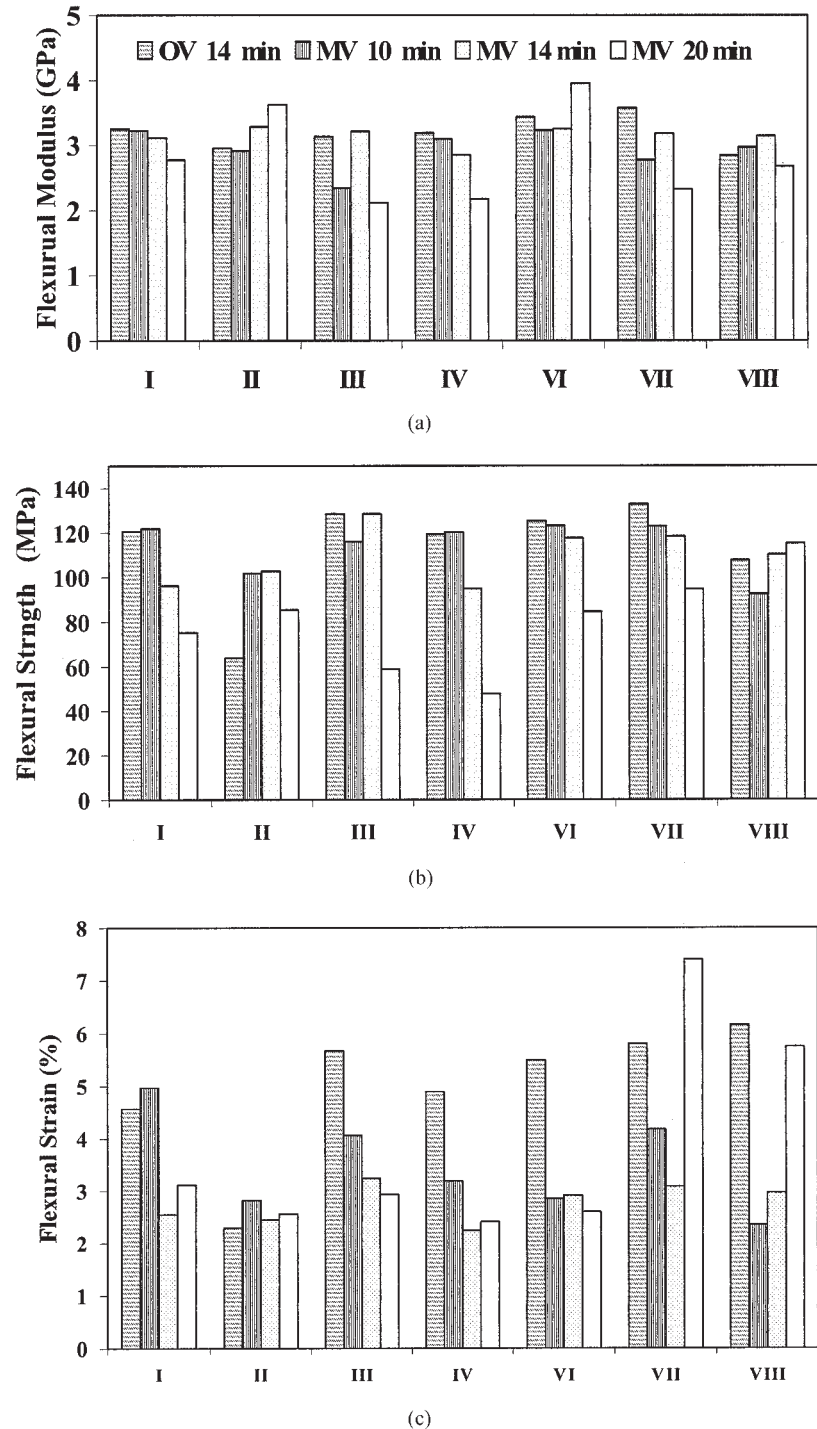
Cured resins were machined to fit the DMTA testing geometry specified by the Rheometric Scientific

DMTA V system (Piscataway, NJ) (ca. 10 mm × 240 mm × 1.5 mm). The testing was performed in a singlecantilever mode at a heating rate of 2°C/min with a strain control of 0.1%. The applied frequencies were 1, 10, and 30 Hz within the temperature range of 30–250°C.  $T_g$  was taken as the temperature at the peak of the  $\tan \delta$  curve in the glass-transition region. The breadth of the glass transition in the  $\tan \delta$  curve was determined as the width across the curve when it dropped to half of its peak values [full width at half-maximum (fwhm)]. The moduli in the glassy and rubbery regions were measured at  $T_g - 30^\circ\text{C}$  and  $T_g + 30^\circ\text{C}$ , respectively.

## RESULTS AND DISCUSSION

### Microwave oven calibration

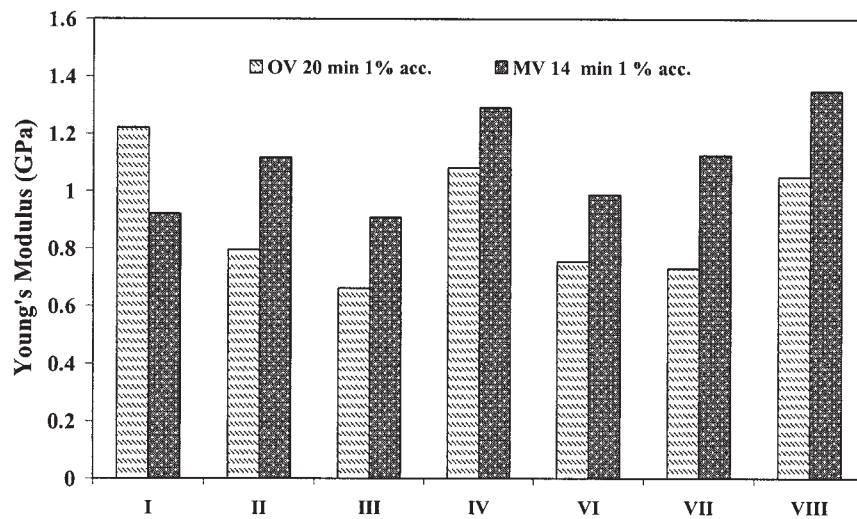
The microwave had 10 power levels. According to the product data sheet, the levels 1 and 10 were the lowest and highest powers (80 and 800 W), respectively. Because the microwave oven used in this study was a domestic one, we measured the magnetron's output power according to the method described by Voss and Madsen.<sup>29</sup> The magnetron's output power at each level is listed in Table IV; the experimental data were lower than those reported by the producer. The equivalent powers derived from the linear regression of experimental data are listed in Table IV and shown in Figure 2. Practically, the output power of the magnetron could be controlled through the adjustment of the period of operation or through the adjustment of the cathode current or magnetic field strength.<sup>17</sup> In home microwave ovens, the magnetron is operated at full power. During a specified time, the current is turned on and off for segments of the period, and the average power is reduced. This on/off type of control is often called duty cycle control.



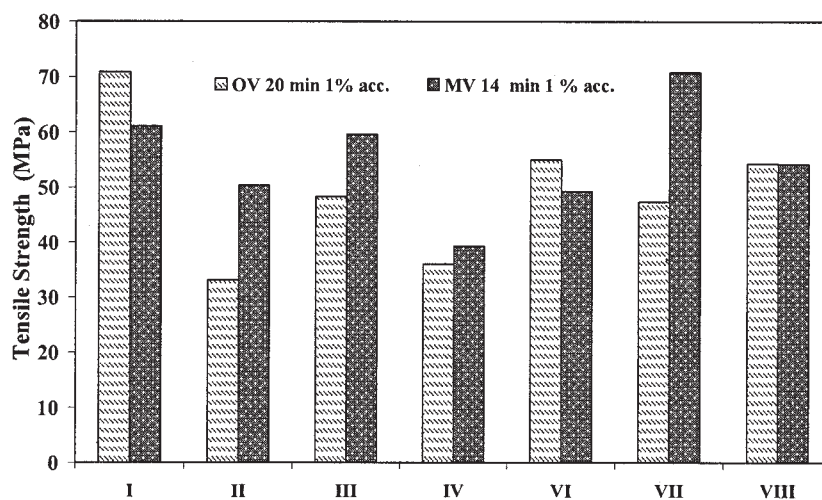
**Figure 5** Flexural properties of the epoxy resins containing 4% accelerator (OV = oven cure, MV = microwave cure): (a) flexural modulus, (b) flexural strength, and (c) flexural strain. The accelerator concentration of resin I was unknown.

One period of the microwave oven used in this study was 17 s. The real heating time of the oven, therefore, was controlled by the setting power. At the setting power of level 3, in one period (17 s), the resins received microwaves for the first 5 s, and then they were heated again after 12 s. At level 4, the actual heating time was 7 s per period. The higher power level had a longer heating

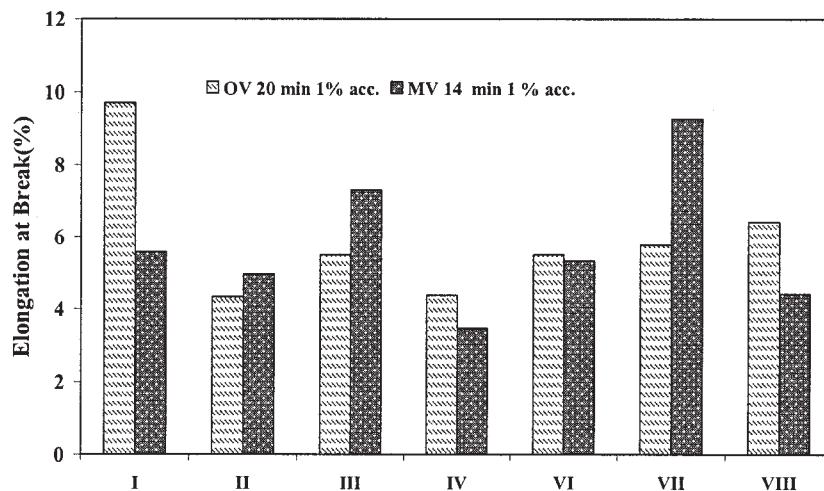
time; that is, the heating times were 14 and 17 s at levels 8 and 10, respectively. Therefore, the actual heating time in the microwave oven was much shorter than the setting time, as described in Table V. This indicates that the output power of the home microwave was governed by the duty cycle control, and the microwave output power depended on the actual heating time.



(a)



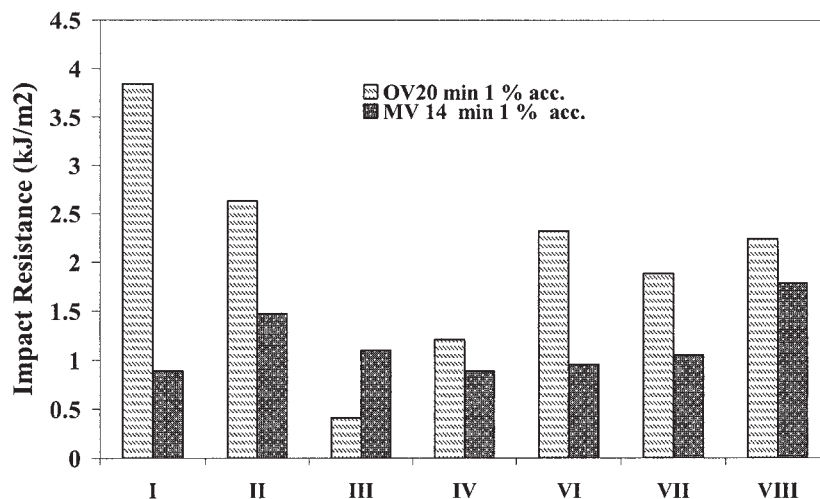
(b)



(c)

**Figure 6** Tensile properties of the epoxy resins containing 1% accelerator (OV = oven cure, MV = microwave cure): (a) Young's modulus, (b) tensile strength, and (c) elongation at break. The accelerator concentration of resin I was unknown.





**Figure 7** Impact strength of the epoxy resins containing 1% accelerator (OV = oven cure, MV = microwave cure). The accelerator concentration of resin I was unknown.

### Ultimate mechanical properties

#### System containing 4% accelerator

The mechanical properties of the epoxy resins containing 4% accelerator are shown in Figures 3–5. Obviously, the effect of the microwave irradiation on the cure of this epoxy–anhydride system depended on the curing agents; this finding is similar to other researchers' work. This study employed three curing times in the microwave oven (10, 14, and 20 min), and eight recipes (Table II) were investigated to determine the mechanical properties. There was no attempt to seek the best mechanical properties and the best recipe. Young's moduli of the oven-cured samples and some microwave-cured samples were in the same range [Fig. 3(a)]. The tensile strengths of resins III, IV, and VI showed significant differences between the oven-cured and microwave-cured samples, whereas those of resins I, II, VII, and VIII were similar [Fig. 3(b)]. The impact resistance of the microwave-cured samples seemed to be higher than or similar to that of the oven-cured samples (Fig. 4), except for resin VI. The flexural modulus and flexural strength of certain microwaved samples were in the same range as those of thermally cured samples (Fig. 5). For resins I and II, the microwave-cured samples showed good mechanical properties like those of the samples cured in the oven, including the tensile properties, impact strength, and flexural properties. Undoubtedly, the mechanical properties of the microwaved samples were strongly dependent on the chemical structure, formulation, and curing time. Therefore, each resin exhibited its own characteristics, and it was difficult to draw a conclusion for all the resins corresponding to other previous works, as stated earlier.<sup>6,7,9–11</sup> We can state that a microwave-cured epoxy with good mechanical properties can be achieved.

#### System containing 1% accelerator

Because the mechanical properties strongly depend on the resin composition, we investigated the effect of the accelerator concentration. By reducing the accelerator concentration to 1%, we had to increase the cure time in the oven to 20 min because the resin could not be cured in a shorter cure time. The cure time in the microwave oven was 14 min or more. We selected the shortest time to minimize the cure time, and we also had a target cure time that was not longer than 20 min. Resin I contained an unknown accelerator. Figures 6–8 present the mechanical properties of the resins containing 1% accelerator. Figure 6 shows that resin I had higher modulus and strength in oven curing, whereas the rest of the resins showed promising properties in microwave curing. The impact strength (Fig. 7), flexural modulus, and strength (Fig. 8) of the oven-cured samples were higher than those of the microwave-cured samples. This indicates that curing the resins with 1% accelerator in the microwave oven for 14 min did not improve the mechanical properties.

#### Comparison under the same heat source

Until now, our results have shown that microwave curing can improve and not improve mechanical properties. It is essential to design the optimal curing conditions for each resin system to obtain the optimal properties. It has been established that the stiffness and impact behavior have an optimum at an 80% epoxy conversion and decrease with higher extents of reaction,<sup>30</sup> and a higher crosslink density lowers the modulus of epoxy.<sup>7</sup> To better understand each property of this system, we compared the mechanical properties of the resins cured under the same heat source. Figures 9–11 show the mechanical properties of resins

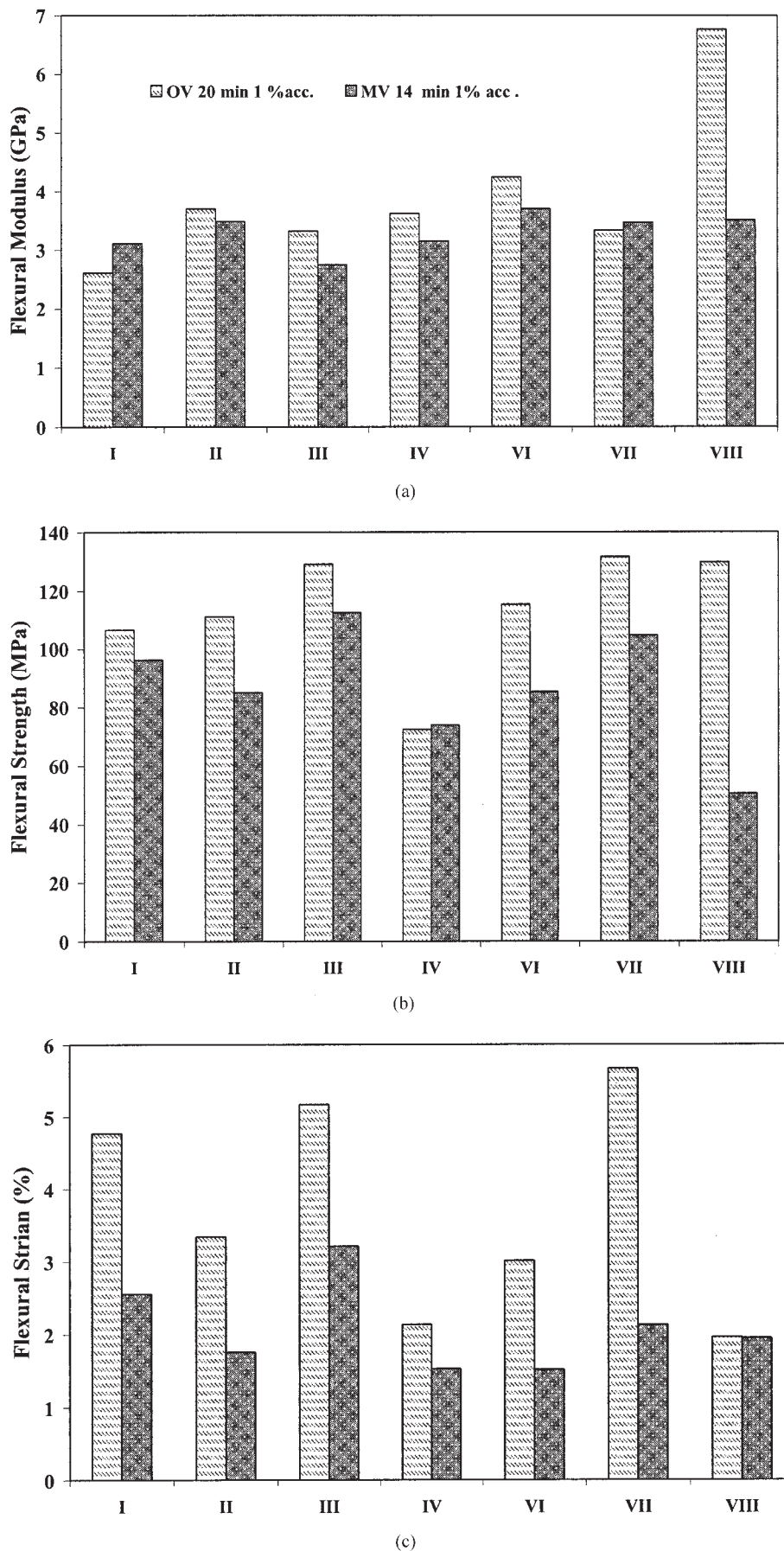
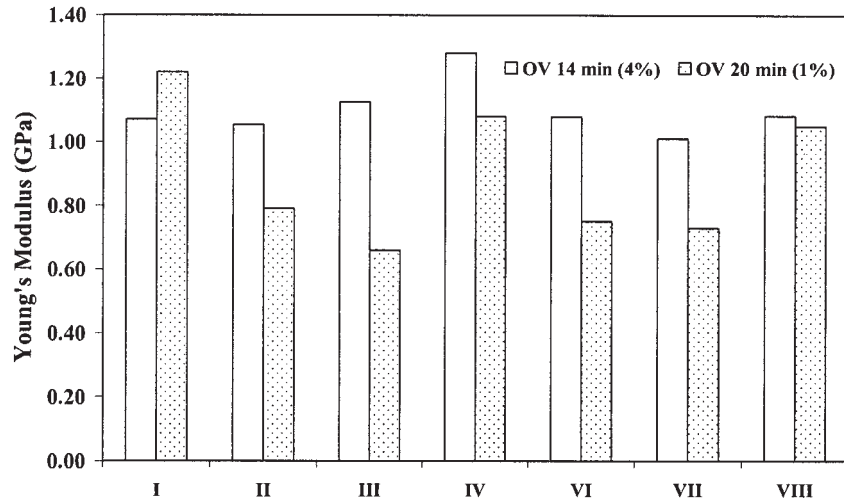
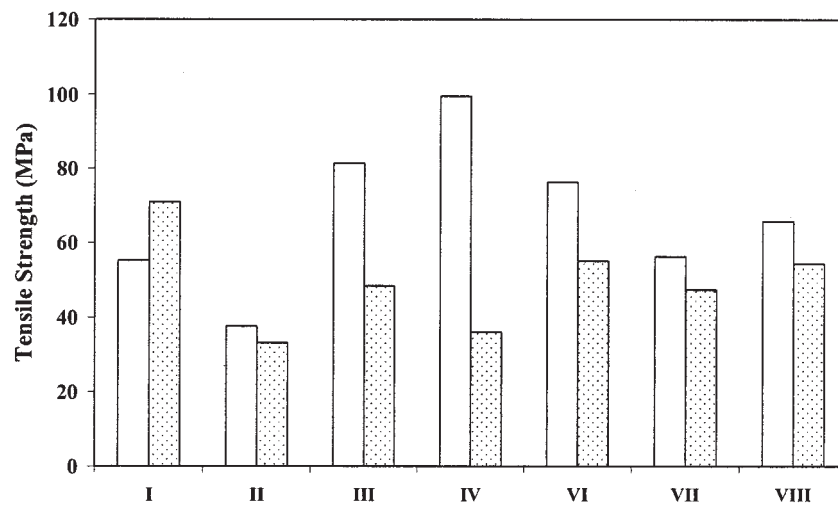


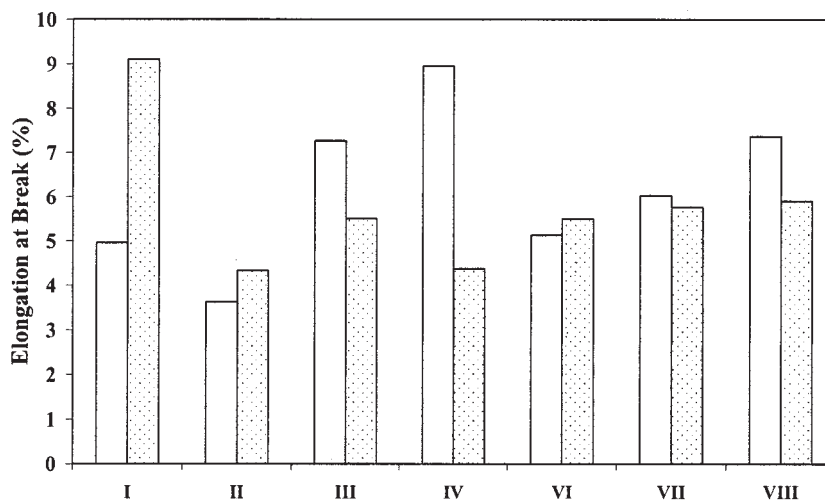
Figure 8 Flexural properties of the epoxy resins containing 1% accelerator (OV = oven cure, MV = microwave cure): (a) flexural modulus, (b) flexural strength, and (c) flexural strain. The accelerator concentration of resin I was unknown.



(a)

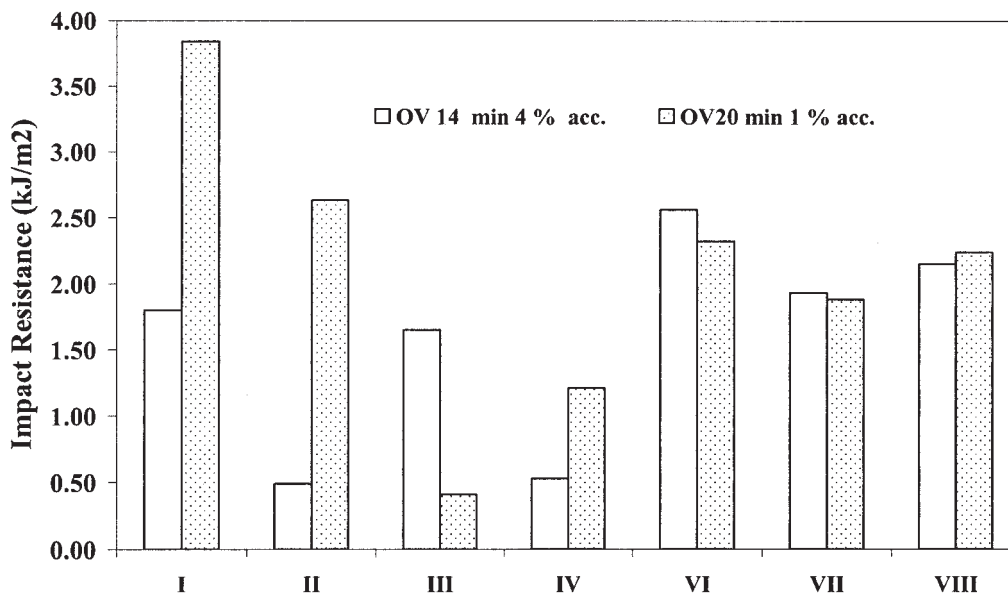


(b)



(c)

**Figure 9** Tensile properties of the epoxy resins containing 1 or 4% accelerator and cured in an oven at 150°: (a) Young's modulus, (b) tensile strength, and (c) elongation at break. The accelerator concentration of resin I was unknown.



**Figure 10** Impact strength of the epoxy resins containing 1 or 4% accelerator and cured in an oven at 150°. The accelerator concentration of resin I was unknown.

cured in the oven for 14 and 20 min. Resin I had higher values of Young's modulus and the tensile and impact strengths for the samples cured at longer time (20 min). In contrast, an improvement in the flexural properties of this resin was obtained with the shorter cure time (14 min). Resins II–VIII were quite complicated because of the different amounts of the accelerator. A higher tensile modulus and tensile strength were derived from the samples cured for 14 min (containing 4% accelerator). The impact strength and flexural properties of these resins showed complex results, except for their flexural moduli, which became higher in the samples cured for 20 min (containing 1% accelerator). Figures 12–14 present the mechanical properties of the microwave-cured samples containing 4 or 1% accelerator. Under the same cure time in the microwave oven (14 min), higher impact and flexural strengths of resins II–VIII were obtained from the resins containing 4% accelerator, whereas higher values of Young's modulus and the flexural modulus were obtained from the resins containing 1% accelerator. These results indicate that each mechanical property had its own requirements. To differentiate those requirements is beyond the scope of this study.

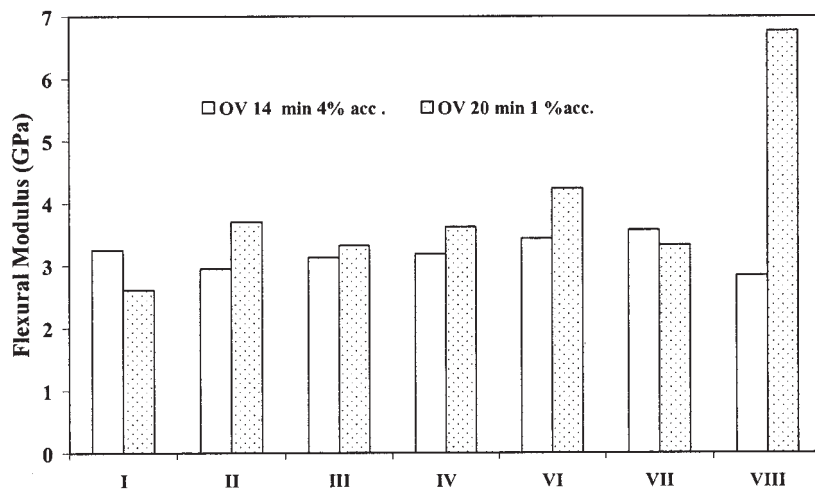
Although there are many articles reporting on microwave-cured epoxy resins,<sup>1–33</sup> few report the mechanical properties of microwaved samples. Microwave-cured epoxy-amine systems show various mechanical properties,<sup>6,7,9–11,15,31</sup> including slight or significant increases in the mechanical properties, strength reduction, and no significant changes in the elastic properties. Most of the microwave-cured resins have been based on an epoxy-amine system; only a few researchers have worked on epoxy-anhydride

systems.<sup>26,33</sup> Zhou et al.<sup>26</sup> reported that microwave-cured epoxy-maleic anhydride resins showed higher compressive and bending strengths than those cured in a thermal oven. They cured epoxy resins for long times (e.g., 1 h for microwave curing and 3 h for thermal curing). We could not compare our results with their results because of differences in many factors, including the microwave oven, hardener, and curing conditions. For our microwave-cured epoxy-anhydride system, we found that microwave curing offered a shorter cure time and equivalent mechanical properties in comparison with oven curing. Each mechanical property could be obtained from the individual optimal curing condition and individual optimal resin composition. This agrees with work of Boey and coworkers.<sup>20,21</sup> They reported that the optimal cure time was dependent on the resin system; the changes in the hardener caused changes in the cure time and  $T_g$ .

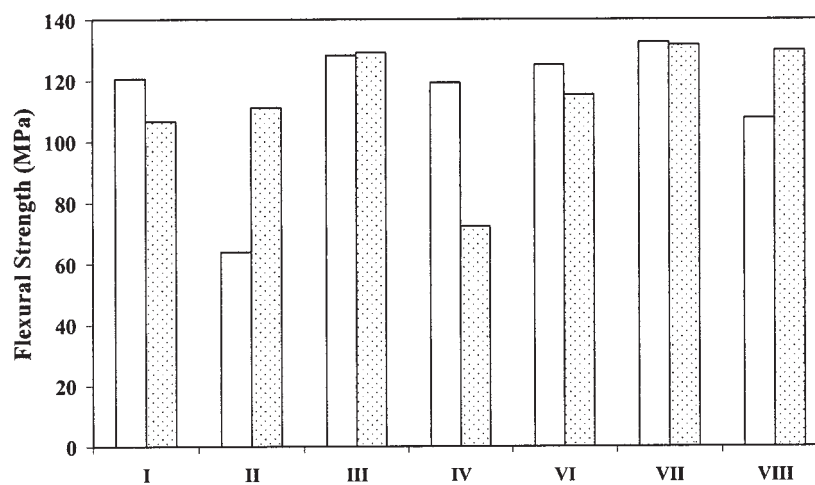
#### Extent of the conversion

To determine  $\chi$  under microwave curing, we investigated all cured samples with the DSC technique. There have been many researchers using DSC to determine the degree of conversion of an epoxy resin from microwave curing<sup>7,18,20,21,30,33</sup> and thermal curing.<sup>40–48</sup> When the samples were not completely cured, the exothermic peak was obtained from the first heating scan.  $\chi$  of the cured samples was calculated as follows:

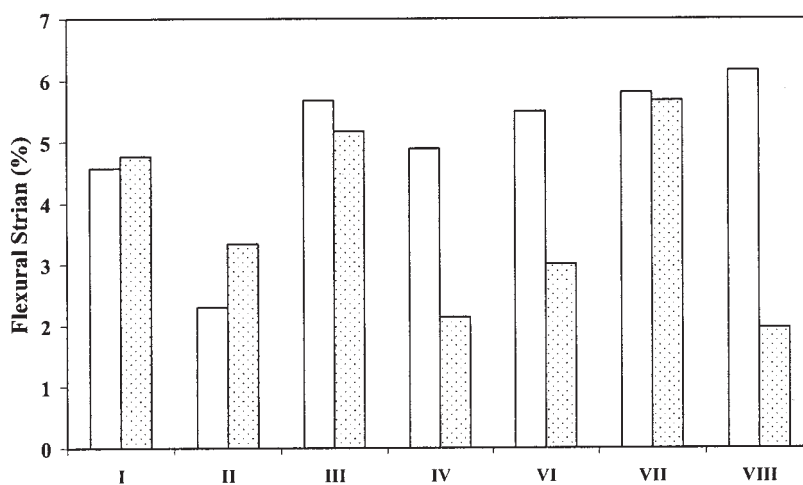
$$\chi(\%) = [1 - (\Delta H_s / \Delta H_f)] \times 100$$



(a)

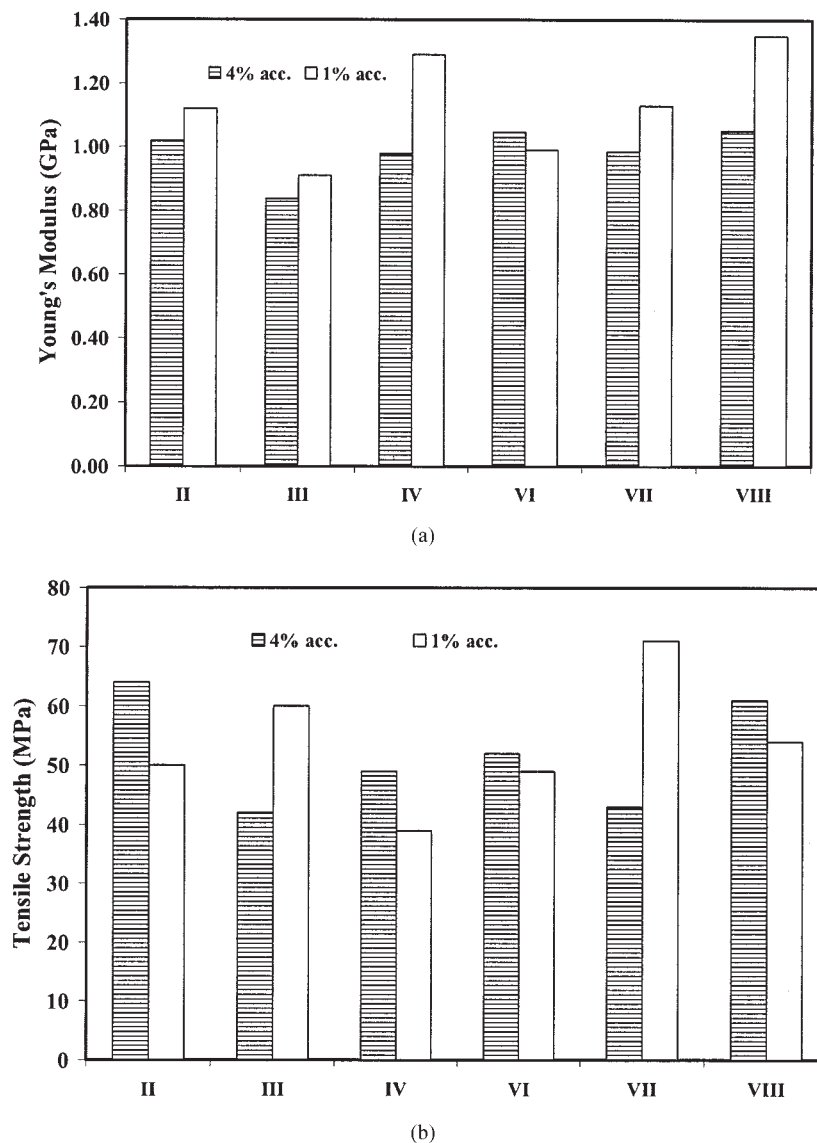


(b)



(c)

**Figure 11** Flexural properties of the epoxy resins containing 1 or 4% accelerator and cured in an oven at 150°: (a) flexural modulus, (b) flexural strength, and (c) flexural strain. The accelerator concentration of resin I was unknown.



**Figure 12** Tensile properties of the epoxy resins containing 1 or 4% accelerator and cured in a microwave oven for 14 min: (a) Young's modulus and (b) tensile strength.

where  $\Delta H_s$  is the heat of reaction of the samples cured in the thermal oven and microwave oven and  $\Delta H_f$  is the heat of reaction of fresh samples cured under the DSC heating scan, representing 100% conversion. The  $\chi$  values of all the cured samples are listed in Table VI. All the samples were cured to more than 90% conversion, except for a few samples. Most samples showed 97% conversion or more. Only oven-cured resins I and IV containing 1% accelerator showed low  $\chi$  values, 87 and 82%, respectively. The complete curing reaction of epoxy resins, determined with DSC, has been established.<sup>18,44,49-51</sup> Particularly, the 100% conversion of microwave-cured epoxy has been reported.<sup>18,44</sup> Obviously, the concentration of the accelerator (1 and 4%) did not have a significant effect on the degree of conversion for the microwave-cured samples. As stated earlier, the microwave output of our microwave

oven was controlled by the on/off current. Therefore, the actual heating time was much shorter than the setting time, as described in Table V. Again, we tabulated the effective cure times (actual heating times) for all the samples in Table VII. Noticeably, the microwave oven exhibited more efficiency in curing than the thermal oven, that is, a shorter cure time for the same or greater degree of conversion. We can state that the microwave showed rate enhancement for curing. Generally, the total process time or cure time should decrease, but the kinetic reaction may or may not change.<sup>15</sup> Changes in the reaction rate and  $T_g$  depend on the resin system.<sup>4,20,21</sup> Boey et al.<sup>18</sup> proposed that microwave curing led to rate enhancement because the curing time in the microwave oven was shorter than that in the thermal oven and different curing agents showed different results.

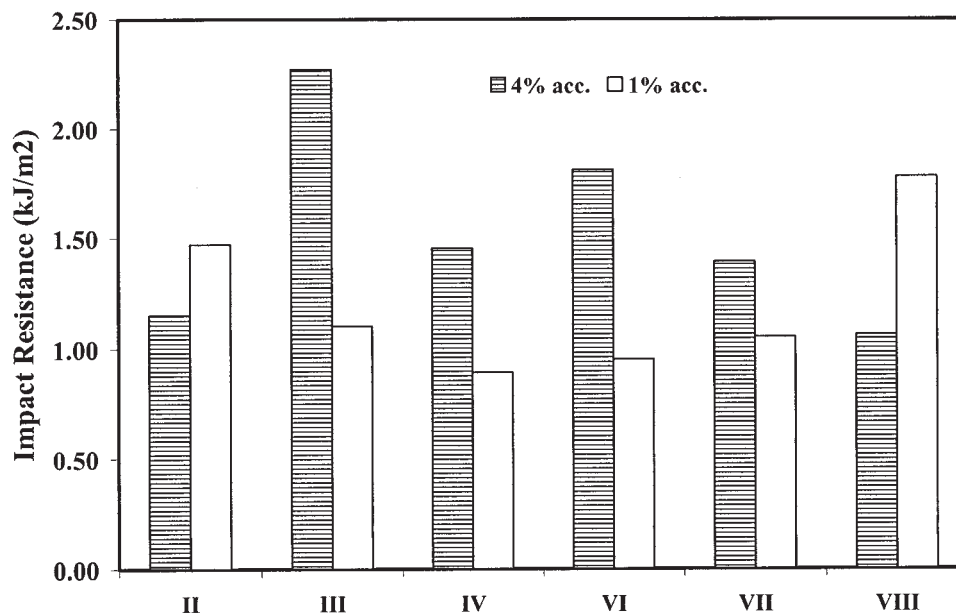


Figure 13 Impact strength of the epoxy resins containing 1 or 4% accelerator and cured in a microwave oven for 14 min.

## DMTA

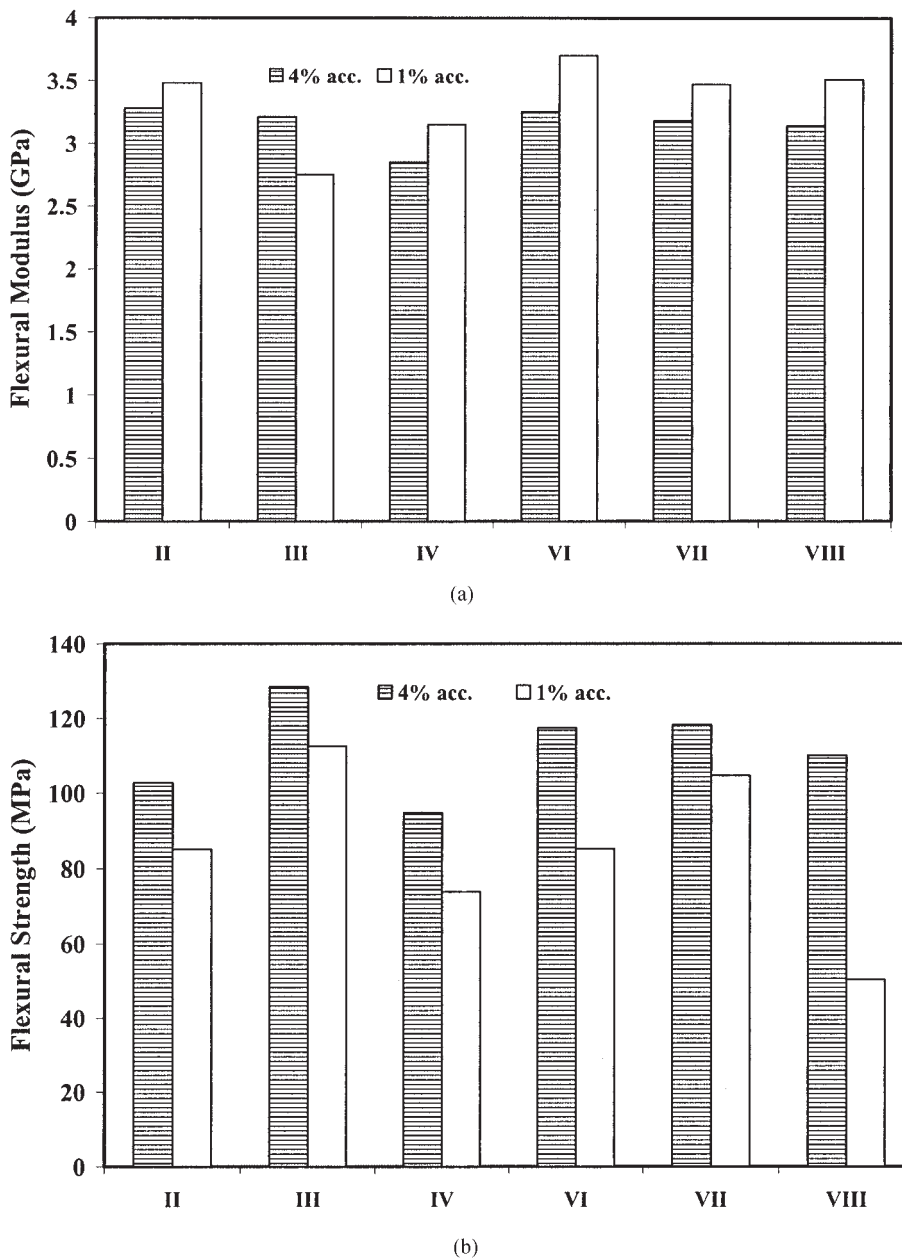
### $\alpha$ Relaxation

DMTA has been used widely to characterize epoxy resins.<sup>52-63</sup> It has been argued<sup>56,63</sup> that some thermosets have a heterogeneous structure with regions of low and high crosslink densities, and this may affect their ultimate properties. Because the breadth of the glass-transition region gives an indication of the range of molecular mobility in the network, studies of the glass transition can provide information about heterogeneity. Table VIII presents DMTA results.  $T_g$  was taken as the maximum of the  $\tan \delta$  curve in the glass-transition region at 1 Hz. The maximum  $\tan \delta$  value corresponded to the peak height of  $T_g$ . The breadth of the glass transition of the  $\tan \delta$  curve was determined as fwhm. Figure 15 presents  $\tan \delta$  curves of resins I and II. They showed normal curves as common resins.

The  $\alpha$ -transition temperatures ( $\tan \delta$ ) of the thermally cured and microwave-cured resins were in the same range, with some deviations, as shown in Table VIII. In theory, the glass-transition region moves to a higher temperature because of the higher crosslink density. Most resins were almost completely cured and showed slight differences in  $\chi$  between thermal and microwave curing, as listed in Table VI, but some resins showed different  $T_g$ 's with different curing systems, as listed in Table VIII. This was also found in the microwave-cured epoxy-amine resin reported by Boey and Yap.<sup>21</sup> The values of  $T_g$  did not correlate with the degree of conversion. They mentioned that the effect of microwave curing with different curing agents on the resulting  $T_g$  was less understood. The rate of the crosslinking reaction was proportional to

the difference between  $T_g$  at that time and the cure temperature. Once  $T_g$  exceeded the curing temperature, that is, vitrification occurred, the reaction substantially stopped, and this limited any further increase in  $T_g$ . It was therefore possible that the theoretical maximum  $T_g$  was not achieved because of a nonoptimal curing process. The maximum  $T_g$  depended on the curing agents and curing conditions.

Table VIII lists the breadth of the  $\tan \delta$  curve (in terms of fwhm). The breadth of the transition region was relatively dependent on the resin formulation and independent of the degree of cure, and all the values were in the same range within the experimental errors. Cook et al.<sup>56</sup> also found the independence of the degree of conversion, and they suggested that the crosslink density per se did not cause broadening. It has been argued<sup>63</sup> that the crosslink heterogeneity is directly reflected in the breadth of the glass transition. The single phase observed in the  $\tan \delta$  curve in this study did not support the existence of a two-phase-structure, crosslink heterogeneity. However, it has been suggested<sup>63</sup> that phase-separated domains are too small to be detected by DMTA. Some conflict in the relationship between fwhm and the crosslink density of cured vinyl ester resins was reported by Scott et al.<sup>63</sup> For each resin formula, the glassy moduli of the thermally cured and microwave-cured resins tended to fall in the same range. This value was slightly higher than Young's modulus, as shown in Figure 3. The crosslink density could be calculated from the rubbery modulus.<sup>57,60,63</sup> The rubbery moduli of microwave and thermally cured resins for each formula were in the same range, except for resins I and III. The DMTA results indicated that our epoxy-anhydride



**Figure 14** Flexural properties of the epoxy resins containing 1 or 4% accelerator and cured in a microwave oven for 14 min: (a) flexural modulus and (b) flexural strength.

resins had similar or only slightly different crosslink densities for both curing systems.

#### Apparent activation energy ( $E_a$ )

$E_a$  of the  $\alpha$  relaxation can be an important clue for identifying associated molecular motions.<sup>2</sup> DMTA spectroscopy was used to establish the changes in the crosslink density and measure the energetics of the  $\alpha$  transition as quantified through  $E_a$ , the activation enthalpy ( $\Delta H^*$ ), and the activation entropy ( $\Delta S^*$ ).<sup>53</sup> The apparent  $E_a$  value for the  $\alpha$  relaxation was calculated<sup>52-56</sup> by means of the Arrhenius relationship from

the slope of a linear plot of the logarithm of the applied frequency ( $\ln f$ ) versus the inverse of the temperature at which the maximum peak of  $\tan \delta$  ( $T_g$ ) appeared as follows:

$$\ln f = \ln A - (E_a/R) \times 1/T_g$$

where  $R$  is the gas constant and  $A$  is a constant.  $\Delta H^*$  and  $\Delta S^*$  were calculated with an Eyring-type relationship:<sup>52,53,62</sup>

$$\ln (f/T_g) = \ln (k/2\pi h) - (\Delta H^*/R) \times 1/T_g - \Delta S^*/R$$

where  $k$  and  $h$  are the gas constant and Planck's constant, respectively.  $\Delta H^*$  was derived from the slope,



**TABLE VI**  
Extent of Conversion of the Cured Samples

| Resin | 1% Accelerator    |             | 4% Accelerator    |                   |
|-------|-------------------|-------------|-------------------|-------------------|
|       | Microwave (%)     | Thermal (%) | Microwave (%)     | Thermal (%)       |
| II    | 97                | 90          | 97                | 97                |
| III   | ≈100 <sup>a</sup> | 93          | ≈100 <sup>a</sup> | 97                |
| IV    | 96                | 82          | ≈100 <sup>a</sup> | ≈100 <sup>a</sup> |
| VI    | 95                | 95          | 98                | 97                |
| VII   | ≈100 <sup>a</sup> | ≈100        | 99                | 96                |
| VIII  | 99                | 97          | 98                | 99                |

Resin I showed degrees of conversion of about 92 and 87% for microwave-cured and thermally-cured samples, respectively. The setting cure time was 14 min for both heat sources.

<sup>a</sup> Exothermic peak was not observed.

**TABLE VII**  
Effective Time for Curing

| Resin | 1% Accelerator  |               | 4% Accelerator  |               |
|-------|-----------------|---------------|-----------------|---------------|
|       | Microwave (min) | Thermal (min) | Microwave (min) | Thermal (min) |
| II    | 6               | 20            | 6               | 14            |
| III   | 4               | 20            | 4               | 14            |
| IV    | 4               | 20            | 4               | 14            |
| VI    | 6               | 20            | 6               | 14            |
| VII   | 4               | 20            | 4               | 14            |
| VIII  | 6               | 20            | 6               | 14            |

Resin I was cured in the thermal oven for 14 min, and the effective time for microwave curing was 6 min.

and  $\Delta S^*$  was derived from the intercept [ $c = \ln(k/2\pi h - \Delta S^*/R)$ ] of a plot of  $\ln(f/T_g)$  versus  $(1/T_g)$ .

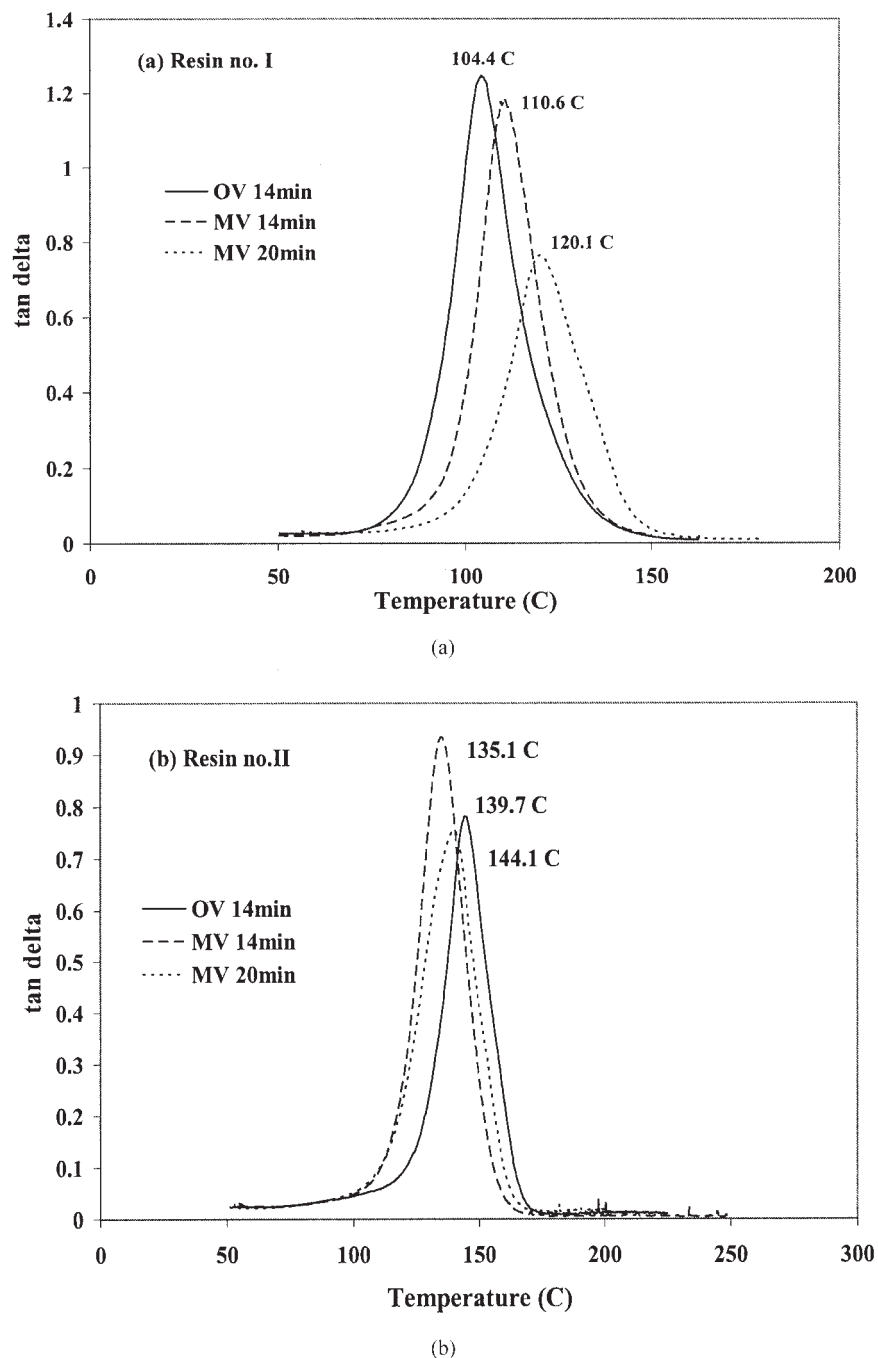
Comparing the two different curing methods, we found that each formula showed not very different  $E_a$

values that fell in the range of 327–597 kJ/mol, as listed in Table IX. The very low  $E_a$  value of resin VI cured in the microwave oven for 20 min may be attributed to the experimental error.  $E_a$  of this epoxy was similar to that of other works, that is, 286–525,<sup>53</sup> 290–508,<sup>54</sup> and 357 kJ/mol.<sup>55</sup> Chen et al.<sup>3</sup> reported that the  $E_a$  values of some microwave-cured polymers [poly(ether ether ketone), nylon 6, nylon 6/12, nylon 12, and poly(ethylene terephthalate)] were in the range of 230–790 kJ/mol. Cook et al.<sup>56</sup> reported that  $E_a$  for the epoxy networks was approximately 500–600 kJ/mol, which was lower than the values of 700–900 kJ/mol but higher than the value of 200 kJ/mol obtained by other researchers for similar networks. This implies that our microwave-cured epoxy-anhydride resin exhibited little difference in the network structure, in comparison with the thermally cured one.

Some insight into the relationship between the structure and stiffness temperature was gained through an estimation of  $E_a$  associated with the  $\alpha$  transition.<sup>53</sup> To the extent that the crosslink density was greater, the hindrance of the surroundings on the motions was more important, the corresponding  $E_a$  barrier was increased, and, finally, the appearance of the motions was delayed to a higher temperature (higher  $T_g$ ). In this work, there seems to be a relationship between  $E_a$  and  $\tan \delta$  for each formula within the limits of the experimental error; the higher  $E_a$  was, the higher  $\tan \delta$  was. However, this relationship was not valid for different formulas, that is, higher  $T_g$ 's but lower  $E_a$ 's. This phenomenon also was reported in previous work.<sup>53,54</sup> Furthermore, Laza et al.<sup>54</sup> showed that crosslink density of the epoxy resin is related to  $T_g$  but is not related to  $E_a$ . Our resin system showed no

**TABLE VIII**  
DMTA Data Measured at a Frequency of 1 Hz for the Resins Containing 4% Accelerator

|                           | I     | II    | III   | IV    | VI    | VII   | VIII  |
|---------------------------|-------|-------|-------|-------|-------|-------|-------|
| Tan $\delta$ (°C)         |       |       |       |       |       |       |       |
| Oven 14 min               | 104.4 | 144.1 | 147.7 | 135.3 | 134.7 | 115.8 | 115.1 |
| Microwave 14 min          | 110.6 | 135.1 | 149.1 | 138.0 | 130.5 | 132.0 | 107.5 |
| Microwave 20 min          | 120.1 | 139.7 | 144.1 | 138.4 | 122.9 | 132.9 | 115.4 |
| Tan $\delta$ maximum      |       |       |       |       |       |       |       |
| Oven 14 min               | 1.240 | 0.781 | 0.525 | 0.846 | 0.773 | 0.652 | 0.667 |
| Microwave 14 min          | 1.185 | 0.734 | 0.534 | 0.915 | 0.832 | 0.649 | 0.875 |
| Microwave 20 min          | 0.763 | 0.756 | 0.539 | 0.943 | 0.866 | 1.010 | 0.859 |
| fwhm of tan $\delta$ (°C) |       |       |       |       |       |       |       |
| Oven 14 min               | 19.25 | 20.61 | 32.29 | 18.82 | 23.67 | 33.67 | 33.02 |
| Microwave 14 min          | 17.58 | 21.43 | 11.83 | 19.67 | 31.18 | 25.15 | 21.42 |
| Microwave 20 min          | 23.45 | 26.20 | 23.51 | 27.54 | 26.68 | 17.56 | 19.50 |
| Glassy modulus (GPa)      |       |       |       |       |       |       |       |
| Oven 14 min               | 2.43  | 1.58  | 1.57  | 1.81  | 2.20  | 2.39  | 1.72  |
| Microwave 14 min          | 1.51  | 1.56  | 1.16  | 1.04  | 1.27  | 1.46  | 1.93  |
| Microwave 20 min          | 1.19  | 1.38  | 1.22  | 1.23  | 0.84  | 1.42  | 1.56  |
| Rubbery modulus (MPa)     |       |       |       |       |       |       |       |
| Oven 14 min               | 24.8  | 15.7  | 16.9  | 16.5  | 18.7  | 14.1  | 10.7  |
| Microwave 14 min          | 14.4  | 17.9  | 15.7  | 14.2  | 13.7  | 16.8  | 11.8  |
| Microwave 20 min          | 14.7  | 13.1  | 26.8  | 16.1  | 11.4  | 14.1  | 13.9  |



**Figure 15**  $\tan \delta$  values of (a) resin I and (b) resin II tested at a frequency of 1 Hz. The numbers indicate the  $\alpha$ -transition temperature (°C) of each sample.

relationship between  $E_a$  and the degree of conversion. This may be attributed to the very close degree of conversion for each formula and a normal large range of  $E_a$ . It has been reported<sup>56</sup> that  $E_a$  may or may not rise with the conversion. As expected, the measured  $E_a$  and enthalpy values were similar in magnitude (Table IX).  $\Delta S^*$  may provide information on the extent of the rearrangements associated with the local motions.<sup>52</sup> Remarkably,  $\Delta S^*$  showed a tendency similar to that of  $E_a$  and the enthalpy (Table IX).  $\Delta S^*$  could be correlated

with the magnitudes of the disorder and cooperativity associated with the transitions involving similar structural units. The very large value of  $\Delta S^*$  represented a substantial degree of long-range cooperativity in the  $\alpha$  transition.

## CONCLUSIONS

This work has shown that the epoxy-anhydride system can be cured with a microwave oven. The me-

TABLE IX  
 $E_a$ ,  $\Delta H^*$ , of and  $\Delta S$  Resins Containing 4% Accelerator

|                       | I   | II   | III | IV   | VI   | VII | VIII |
|-----------------------|-----|------|-----|------|------|-----|------|
| $E_a$ (kJ/mol)        |     |      |     |      |      |     |      |
| Oven 14 min           | 365 | 575  | 315 | 438  | 521  | 391 | 354  |
| Microwave 14 min      | 327 | 355  | 417 | 508  | 388  | 426 | 597  |
| Microwave 20 min      | 406 | 474  | 458 | 515  | 200  | 442 | 459  |
| $\Delta H^*$ (kJ/mol) |     |      |     |      |      |     |      |
| Oven 14 min           | 363 | 571  | 311 | 435  | 518  | 388 | 351  |
| Microwave 14 min      | 324 | 352  | 413 | 504  | 384  | 423 | 594  |
| Microwave 20 min      | 402 | 471  | 455 | 512  | 197  | 439 | 456  |
| $\Delta S^*$ (J/mol)  |     |      |     |      |      |     |      |
| Oven 14 min           | 728 | 1139 | 508 | 832  | 1037 | 765 | 673  |
| Microwave 14 min      | 613 | 630  | 749 | 996  | 717  | 813 | 1328 |
| Microwave 20 min      | 790 | 911  | 857 | 1012 | 267  | 850 | 941  |

chanical properties of the microwaved samples (resins I and II) were comparable to those of thermally cured samples. The optimization of the electromagnetic treatment was required. The rate enhancement of curing was obtained from the microwave curing. The changes in the mechanical properties were associated with the resin formulation and curing conditions.  $T_g$ ,  $E_a$ , and other DMTA results indicated slight differences in the three-dimensional epoxy structures between the thermal and microwave curing.

The authors thank Thai Composites Co., Ltd., for supplying the chemicals.

## References

- Jow, J.; Hawley, M. C.; Finzel, M.; Kern, T. *Polym Eng Sci* 1988, 28, 1450.
- Chen, M.; Siochi, E. J.; Ward, T. C.; Mcgrath, J. E. *Polym Eng Sci* 1993, 33, 1092.
- Chen, M.; Hellgeth, J. W.; Siochi, E. J.; Ward, T. C.; Mcgrath, J. E. *Polym Eng Sci* 1993, 33, 1122.
- Wei, J.; Hawley, M. C.; Delong, J. D. *Polym Eng Sci* 1993, 33, 1132.
- Livi, A.; Levita, G.; Rolla, P. A. *J Appl Polym Sci* 1993, 50, 1583.
- Chen, M.; Hellgeth, J. W.; Ward, T. C.; Mcgrath, J. E. *Polym Eng Sci* 1995, 35, 144.
- Jordan, C.; Galy, J.; Pascault, J. P. *Polym Eng Sci* 1995, 35, 233.
- Wei, J.; Hawley, M. C.; Demeuse, M. T. *Polym Eng Sci* 1995, 35, 461.
- Jacob, J.; Chia, L. H. L.; Boey, F. Y. C. *J Mater Sci* 1995, 30, 5321.
- Jacob, J.; Chia, L. H. L.; Boey, F. Y. C. *Polym Test* 1995, 14, 343.
- Bai, S. L.; Djafari, V.; Andreani, M.; Francois, D. *Eur Polym J* 1995, 9, 875.
- Wei, J.; Shidaker, T.; Hawley, M. C. *Trends Polym Sci* 1996, 4, 18.
- Dabek, R. *Polym Eng Sci* 1996, 36, 1065.
- Jullien, H.; Petit, A.; Merienne, C. *Polymer* 1996, 37, 3319.
- Mijovic, J.; Corso, W. V.; Nicolais, L.; Ambrosio, G. D. *Polym Adv Technol* 1998, 9, 231.
- Hedreul, C.; Galy, J.; Dupuy, J.; Delmotte, M.; More, C. *J Appl Polym Sci* 1998, 68, 543.
- Thostenson, E. T.; Chou, T. W. *Compos A* 1999, 30, 1055.
- Boey, F. Y. C.; Yap, B. H.; Chia, L. *Polym Test* 1999, 18, 93.
- Fu, B.; Hawley, M. C. *Polym Eng Sci* 2000, 40, 2133.
- Boey, F. Y. C.; Rath, S. K. *Adv Polym Technol* 2000, 19, 194.
- Boey, F. Y. C.; Yap, B. H. *Polym Test* 2001, 20, 837.
- Hedeul, C.; Galy, J.; Dupuy, J.; Delmotte, M.; More, C. *J Appl Polym Sci* 2001, 82, 1118.
- Hill, D. J.; George, G. A.; Rogers, D. G. *Polym Adv Technol* 2001, 12, 169.
- Hill, D. J.; George, G. A.; Rogers, D. G. *Polym Adv Technol* 2002, 13, 353.
- A'Arrigo, A. C.; Focher, B.; Pellancan, G. C.; Cosentino, C.; Torri, G. *Macromol Symp* 2002, 180, 223.
- Zhou, J.; Shi, C.; Mei, B.; Yuan, R.; Fu, Z. *J Mater Process Technol* 2003, 137, 156.
- Boey, F. Y. C.; Rath, S. K. *Adv Polym Technol* 2000, 19, 194.
- Alazard, P.; Palumbo, M.; Gourdenne, A. *Macromol Symp* 2003, 199, 59.
- Voss, W. A. G.; Madsen, T. G. *J Microwave Power Electro* 1987, 22, 209.
- Jordan, C.; Galy, J.; Pascault, J. P. *J Appl Polym Sci* 1992, 46, 859.
- Bogdal, D.; Penczek, P.; Pielichowski, J.; Prociak, A. *Adv Polym Sci* 2003, 163, 193.
- Galema, S. A. *Chem Soc Rev* 1997, 26, 233.
- Acierno, D.; Frigione, M.; Fiumara, V.; Napoli, D.; Pinto, I. M.; Ricciardi, M. *Mater Res Innovat* 1998, 2, 28.
- Degamber, B.; Fernando, G. F. *J Appl Polym Sci* 2003, 89, 3868.
- Nightingale, C.; Day, R. J. *Compos A* 2002, 33, 1021.
- Ellis, B. *Chemistry and Technology of Epoxy Resins*; Chapman & Hall: London, 1993.
- Espuche, E. U.; Gerard, J. F.; Pascault, J. P.; Reffo, G.; Sautereau, H. *J Appl Polym Sci* 1993, 47, 991.
- Zhang, Z.; Beatty, E.; Wong, C. P. *Macromol Mater Eng* 2003, 288, 365.
- Park, W. H.; Lee, J. K. *J Appl Polym Sci* 1998, 67, 1101.
- Laref, F. H.; Mouzali, M.; Abadie, M. J. M. *J Appl Polym Sci* 1999, 73, 2089.
- He, Y.; Moreira, B. E.; Overson, A.; Nakamura, S. H.; Bider, C.; Briscoe, J. F. *Thermochim Acta* 2000, 357, 1.
- Gumen, V. R.; Jones, F. R.; Attwood, D. *Polymer* 2001, 42, 5717.
- Mauri, A. N.; Riccardi, C. C. *J Appl Polym Sci* 2002, 85, 2342.
- Torre, L.; Frulloni, D.; Kenny, J. M.; Manferti, C.; Camino, G. *J Appl Polym Sci* 2003, 90, 2532.
- Ivankovic, M.; Incarnato, L.; Kenny, J. M.; Nicolais, L. *J Appl Polym Sci* 2003, 90, 3012.
- Zhou, S.; Hawley, M. C. *Compos Struct* 2003, 61, 303.
- Rocks, J.; George, G. A.; Vohwinkel, F. *Polym Int* 2003, 52, 1758.
- Park, S. J.; Seo, M. K.; Lee, J. R. *J Polym Sci Part B: Polym Phys* 2004, 42, 2419.

49. Mauri, A. N.; Riccardi, C. C. *J Appl Polym Sci* 2002, 85, 2342.
50. Zhou, S.; Hawley, M. C. *Compos Struct* 2003, 61, 303.
51. Park, S. J.; Seo, M. K.; Lee, J. R. *J Polym Sci Part B: Polym Phys* 2004, 42, 2419.
52. Cukierman, S.; Halary, J. L.; Monnerie, L. *Polym Eng Sci* 1991, 31, 1476.
53. Dyakonov, T.; Chen, Y.; Holland, K.; Drbohlav, J.; Burns, D.; Belde, V. D.; Seib, L.; Soloski, E. J.; Khun, J.; Mann, P. J.; Stevenson, W. T. K. *Polym Degrad Stab* 1996, 53, 217.
54. Laza, J. M.; Julian, C. A.; Larrauri, E.; Leon, L. M. *Polymer* 1998, 40, 35.
55. Wingard, C. D. *Thermochim Acta* 2000, 357, 293.
56. Cook, W. D.; Scott, T. F.; Tjevenon, S. Q.; Forsythe, J. S. *J Appl Polym Sci* 2004, 93, 1348.
57. Guerrero, P.; Caba, K. D. L.; Valea, A.; Corcuera, M. A.; Mondragon, I. *Polymer* 1996, 37, 2195.
58. Charlesworth, J. M. *Polym Eng Sci* 1988, 28, 221.
59. Barral, L.; Cano, J.; Lopez, J.; Bueno, I. L.; Nogueira, P.; Ramirea, C.; Torres, A.; Abad, M. J. *Thermochim Acta* 2000, 344, 137.
60. Park, S. J.; Lee, H. Y.; Han, M.; Hong, S. K. *J Colloid Interface Sci* 2004, 271, 288.
61. Simon, S. L.; Mckenna, G. B.; Sindt, O. *J Appl Polym Sci* 2000, 76, 495.
62. Dargent, E.; Kattan, M.; Cabot, C.; Lebardy, P.; Ledru, J.; Grenet, J. *J Appl Polym Sci* 1999, 74, 2716.
63. Scott, T. F.; Cook, W. D.; Forsythe, J. S. *Eur Polym J* 2002, 38, 705.