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Mechanical Properties and Dynamic Mechanical Thermal Analysis of Microwave-Cured Epoxy Resin*

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Abstract

The purpose of the present work is to replace the curing system of epoxy-anhydride from thermal oven to microwave oven. The present work shows it is able to cure the new epoxy-anhydride system by using the microwave oven. Mechanical properties of the microwaved samples is comparable to those of conventional samples. Glass transition temperature and activation energy indicate similar crosslinking density derived from different curing systems.

Introduction

In conventional thermal processing, energy is transferred to the materials through convection, conduction, and radiation of heat from the surface of the materials. In contrast, microwave energy is delivered directly to the materials through the molecular interaction with the electromagnetic field. In heat transfer, energy is transferred due to thermal gradients, but microwave heating is the transformation of electromagnetic energy to thermal energy and is energy conversion, rather than heat transfer. In microwave processing, energy is supplied by an electromagnetic field directly to the materials. This results in rapid heating throughout the materials thickness with reduced thermal gradients. Volumetric heating can also reduce processing time and save energy. The microwave field and the dielectric response of a material govern its ability to heat with microwave energy. There has been much research in the area of microwave processing for

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polymers and polymer matrix composites [1-10]. A major barrier in the use of thermosetting composites in many applications is the long cure and postcure processing time required to achieve the required mechanical properties. The ability to process polymeric materials with microwave depends on the dipole structure, frequency of processing, temperature, and additives or fillers included with the polymers.

In the present work, we report the results of an experimental study of epoxy-anhydride resins cured in a domestic microwave oven. Mechanical properties and dynamic mechanical thermal analysis of the microwave cured resins have been compared to those of the conventional thermal cured resins. This work is applied to the glass fiber reinforced epoxy composites, and all chemicals used are industrial grade.

Experiment

Materials

Chemicals used are listed in Table1. Two types of hardeners were employed: methyltetrahydrophthalic anhydride (MTHPA) and methylhexahydrophthalic anhydride (MHHPA). Accelerators used include tris-2,4,6 dimethyl aminomethyl phenol (DMP), 2-ethyl-4-methyl imidazole (EMI) and N-benzyldimethylamine (BDMA). MTHPA1 contains an unknown accelerator, while MTHPA2 and MHHPA have no accelerator.

Table 1. Characteristics of the precursors

Chemical	Grade	Supplier
Epoxy (DGEBA)	D.E.R® 331	Dow Chemical Co.
MTHPA1	Lindried® 46QC	Lindau Chemicals Co.
MTHPA2	NT	LonzaSpa Co.
MHHPA	SW	LonzaSpa Co.
DMP	Ancamine® K54	Anchor Chemical Ltd.
EMI	Imicure® EMI24	Air Products and Chem. Inc
BDMA	purum (> 98%)	Fluka

Sample preparation.

Epoxy was mixed with a hardener (100:80 wt/wt) and an accelerator (4 phr of epoxy). All chemicals used are commercial grade and used as received. Sample designation and composition are listed in Table 2. After well mixing, air bubbles were released from the resin before poring into a mold. A chromium coated steel plate was used as a mold for thermal curing, while a teflon mold was used for microwave curing. MEMMERT® Universal oven was employed for thermal curing. Microwave curing was performed in the domestic microwave oven, SANYO® EMX412, at the frequency of 2.45 GHz. The microwave power used for curing resins was selected based on physical performance of cured samples. No air bubbles and no burning were criteria. The optimum condition for resins I, II. VI and VIII is the level-4 power, while resins Ill, IV and VII were cured at the level-3 power. Microwave curing were operated at 10, 14 and 20 min. Condition for thermal curing was set at 150°C for 14 min.

Table 2. Sample designation and its composition

Code	Hardener	Accelerator
I	MTHPA I	unknown
II	MHHPA	DMP
III	MHHP A	EMI
IV	MHHPA	BDMA
VI	MTHAP2	DMP
VII	MTHPA2	EMI
VIII	MTHPA2	BDMA

Mechanical properties.

Tensile properties, flexural properties (three-point bending) and notched Izod impact resistance were tested according to ASTM D638 (type I), ASTM D790 and ASTM D256, respectively. Tensile testing was conducted at a tension speed of 5 mm./min. and a gauge length of 50 mm. Three-point bending test was executed at a speed of 8 mm/min with a span width of 25 mm. whereas the specimen dimension was 25 x 50 mm. All specimens thickness were in the

range of 1.5 mm.

Dynamic mechanical thermal analysis. (DMTA)

Cured resins were machined to fit the DMTA testing geometry specified by the Rheometric Scientific® DMTA V system (about 10 mm x 240 mm x 1.5 mm). Testing was operated in single cantilever mode at a heating rate of 2 °C/min and under a strain control of 0.1 %. The frequencies were 1, 10 and 30 Hz within the temperature range between 30 - 250°C

Results and discussion

Microwave oven calibration.

Since the microwave oven used in this study is the cooking oven, therefore we calibrated the power of each setting condition as suggested in [11]. This microwave oven has 10 power levels, the level 1st and 10th are the lowest and the highest power respectively (80 and 800 watt), according to the product data sheet. The equivalent power obtained from such calibration method is listed in Table 3. In addition, this microwave oven is set a cycle time (on-off heating time) for 17 sec. At level 3, the magnetron works for 5 sec and shows no function for 12 sec. At level 4, actual time for heating is 7 sec. Therefore, the actual heating time in the microwave oven is much lower than the set time as described in Table 3.

Table 3. Calibration data of the microwave oven

Level	Equivalent power (watt)	Set time (min)	Actual heating time (min)
3*	207	10	3
		14	4
		20	6
4*	276	10	4
		14	6
		20	8

*equals to 30% and 40% of 800 watt respectively, according to product data sheet.

Mechanical properties.

There are few reports comparing the mechanical properties of the microwaved sample

with the conventionally treated sample. There have been conflicting results on this topic [3,4,6,7,10]. Microwave cured epoxy-amine system showed various mechanical properties, including slight or significant increase in mechanical properties, strength reduce, and no significant changes in the elastic properties. In the present work, the microwaved samples also showed variety in mechanical properties as shown in Figure 1-5. Figure I and Figure 2 represent Young's modulus and tensile strength of the resins cured in the thermal oven and microwave oven. Young's moduli of the oven cured samples and some microwave cured samples fall in the same range. Tensile strength of resin Ill, IV and VI shows significant difference between oven cured and microwave cured samples. Impact resistance of microwave cured samples seems to be higher or similar to that of the oven cured samples (Figure 3), except resin VI. Flexural modulus and flexural strength of certain microwaved samples are in the same range of those of thermal cured samples (Figure 4 and Figure 5). Keep in mind, this study employed 3 curing times in the microwave oven and 8 recipes were investigated. Undoubtedly, mechanical properties of the microwaved samples are strongly dependent of chemical structure, formulation, and curing time. Therefore, each resin exhibits its own characteristics, and it's difficult to draw a conclusion for all resins, similarly to other previous works as stated earlier [3,4,6,7,10]. The present work aimed to make a comparison between the microwave and oven curing, but not looking for the best formulation.

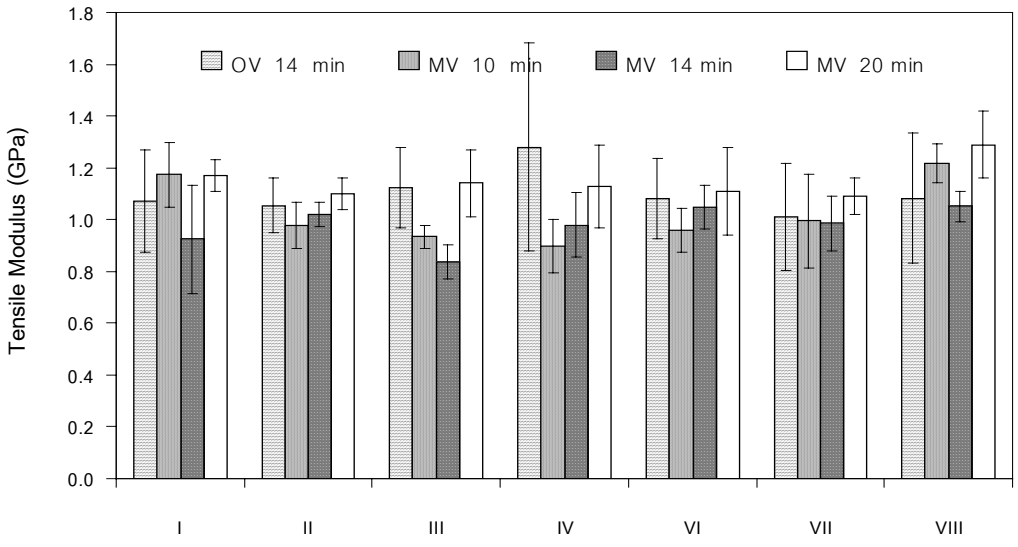

Figure 1. Young's modulus of cured resin

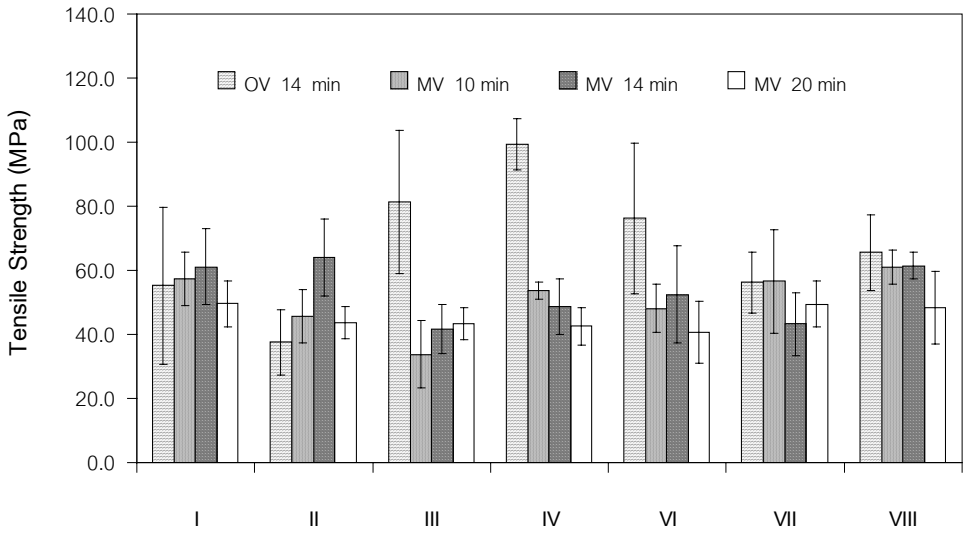

Figure 2. Tensile strength of cured resins

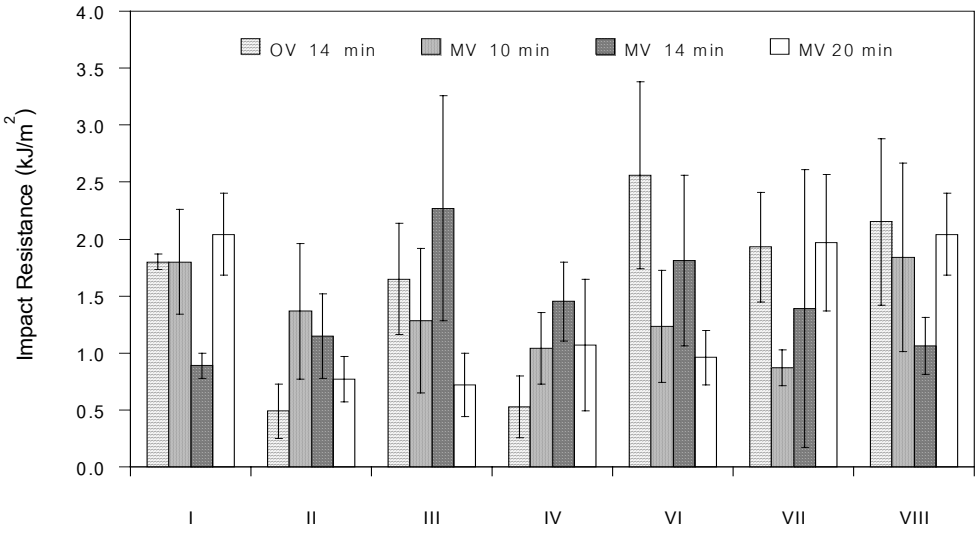

Figure 3. Impact resistance of cured resins

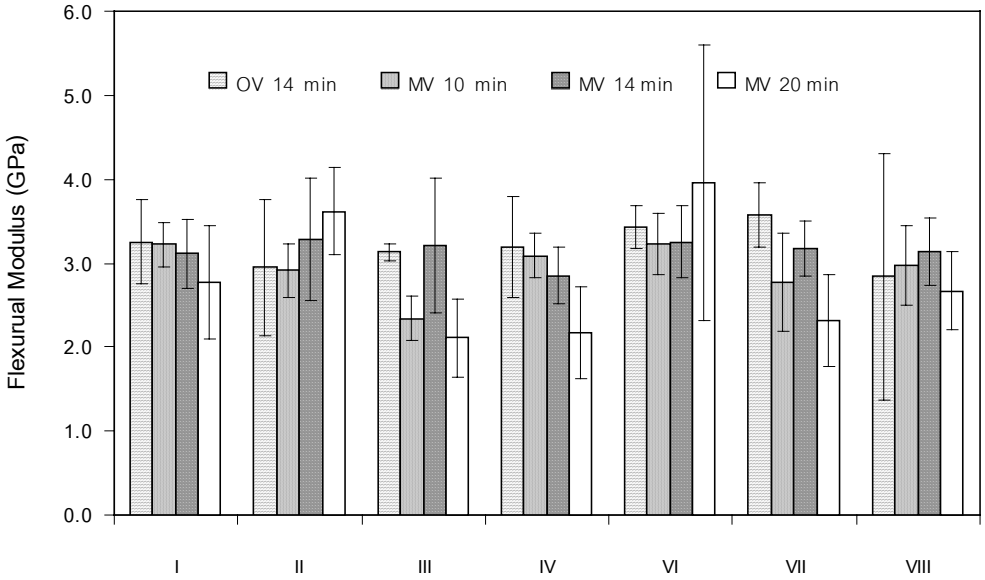

Figure 4. Flexural modulus of cured resins

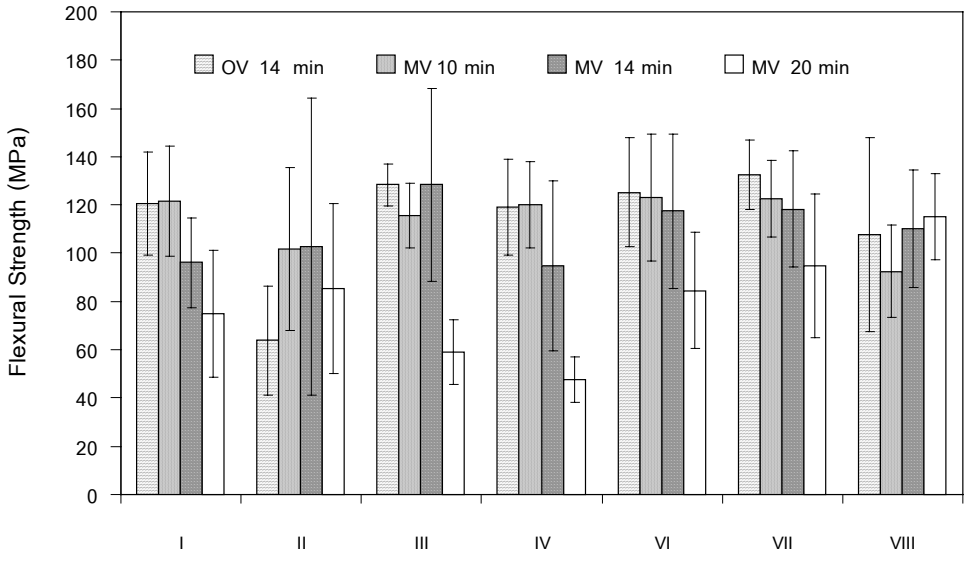

Figure 5. Flexural strength of cured resins.

Glass transition (T_g) and activation energy (E_a)

Tg's of resins characterized at the trequency of 1 Hz are tabulated in Table 4. Tg's of the microwaved samples cured at 14 min and 20 min are closed to T_g's of those cured in the thermal oven. This indicates similar degree of conversion for samples under different curing systems. Apparent activation energy (E_a) was calculated by plotting ln (f_{app}) against $1/T_{max}$, assuming an Arrhenius type relationship to hold between f_{app}, the applied trequency, and T_{max}, the temperature which corresponds to the maximum in tan δ at the frequency f_{app} [12-14]. E_a is obtained from the slope of the curve followed the relationship described below :

$$\ln(f_{app}) = \ln A - (E_a/R).\ 1/T_{max}$$

Some insight into the relationship between structure and stiffness temperature was gained through estimation of activation energy associated with the a. transition [12]. Comparing two different curing methods, each resin shows similar activation energy and falls in the same range of other works, i.e. 389 - 516 kJ/mol [12], 281 - 508 kJ/mol [13] and 357 kJ/mol [14]. This indicates that cross linking density of microwaved samples and thermal cured samples in the present work are similar. Resin IV shows different activation energy among three samples, which may be due to experimental error.

Table 4. T_g obtained from DMTA tested at 1 Hz and activation energy

Code	T_g (°C)			E_a (kJ/mol)		
	OV14	MV14	MV20	OV14	MV14	MV20
I	104	113	115	365	327	267
II	144	148	153	575	355	474
III	148	162	161	315	417	458
IV	135	141	145	438	151	712
VI	135	141	144	521	388	200
VII	116	124	127	391	180	442
VIII	115	123	128	354	597	455

Conclusion

The present work shows that it is able to cure the new epoxy-anhydride system by using the microwave oven. Mechanical properties of the microwaved samples is comparable to those of conventional samples. Glass transition temperature and activation energy indicates similar crosslinking density derived from different curing system.

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