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DIELECTRIC AND TEMPERATURE MEASUREMENTS DURING MICROWAVE CURING OF EPOXY IN A SWEEPING RESONANT CAVITY

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SUMMARY

A TM_{012}-mode cylindrical cavity was mechanically tuned to critically couple with a microwave circuit at 3.2 GHz. A fluoroptic temperature sensing device was used to monitor temperature in the microwave environment. Stoichiometric mixtures of epoxy (DER 332) and amine (DDS) were heated in this sweeping resonant cavity for curing times of 10 and 30 minutes, respectively. On-line temperature and dielectric properties versus time profiles were measured during the curing process. The dielectric properties versus temperature were also measured during cooling. Thereafter, the extent of cure of epoxy was determined by Differential Scanning Calorimeter.

INTRODUCTION

Epoxy Resins are one example of a class of materials known as thermosetting resins. Thermosetting resins are liquid materials that are converted to solids by the addition of heat. The conversion of liquid to solid is brought about small chain polymer molecules reacting with curing agents or each other to form a crosslinked molecular network. Epoxy resins contain epoxide groups which react via a ring-opening mechanism. A common epoxy/curing agent system is a DGEBA (Diglycidyl Ether Bisphenol A)/Amine system. The materials in this study are a difunctional DGEBA resin (DER 332) and a tetrafunctional curing agent (Diaminodiphenylsulfone, DDS). Functionality of resin or curing agent is determined by the number of reactive groups per molecule. The crosslinking occurs through reaction of terminal (chain-ending) epoxy groups with amine groups, and subsequent reaction of epoxy groups with hydroxyl groups formed during the reaction. The progress of the reaction is defined in terms of extent of cure or percentage of available epoxide groups reacted.

Recent research on epoxy cure technology has been focused either on determination of extent of cure by measurement of dielectric properties or on simple microwave curing. Research on dielectric measurement is motivated by the desire to monitor the extent of cure in thermal heating processes. Several measurements of dielectric properties of epoxy samples have been reported between 0.1 Hz and 10 MHz using electrodes (1), a HP low frequency impedance analyzer (2), and microelectrodes (3,4). Also, dielectric measurements have been made within the microwave frequency range using wave guides (5) and transmission lines (6). A summary of results on dielectric measurement is shown in Table 1. Microwave curing of thermosetting resins has been investigated in wave guides (7,8) and multimode microwave ovens (6,9). Gourdenne (7) used a TE_{01} wave guide operated at 2.45 GHz to study temperature/time profiles of DGEBA type epoxy cured with DDM (diaminodiphenylmethane) at different initial power inputs of 40, 60, 80, and 100W to demonstrate that higher microwave power caused faster polymerization and sharper temperature gradients. Karmazsin (8) used a 2.45 GHz TE_{10} wave guide along with a 75W continuous wave energy power level and an equivalent 75W (150W with 50% cyclic ratio) pulsed wave energy power level to investigate temperature/time profiles of AY103/HY 991 epoxy resins. Wilson (6) studied two epoxy/curing agent systems: (1) 100 parts of Epon 828 to 49 parts of T-403 and (2) 100 parts of Epon 828 to 20 parts of Z cured in a conventional microwave oven at 2.45 GHz with two power levels of 245 and 700W to investigate the temperature/time profiles during microwave curing. Strand (9) compared the temperature/time profiles of the thermal cure at oven temperatures of 66, 93, 121, 149, and 177° C to the conventional 2.45 GHz microwave cure at various power levels of 0.75, 1.5, 2.25, and 6 KW for epoxies. These experiments indicated that quick microwave heating initiated the rapid increase in temperature slope at the lower temperature and then heat produced by the exothermic curing reaction significantly increased the temperature slope. The cure time of epoxy by microwave heating was much less than that by thermal heating. The heating mechanism was also different between microwave curing and thermal curing. The microwave energy directly heated the polymer but the thermal energy heated the mold first and transfered the heat into polymers. These experiments showed that fast cure and high efficiency of energy utilization can be obtained by microwave curing compared to thermal curing.

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The primary objective of this study is to explore the use of a microwave single-mode resonant cavity in conjunction with fluoroptic temperature measurement to process epoxy and to on-line monitor the process. A single mode cavity is used for ease of diagnostics. Since a single-mode resonant cavity is used, the dielectric properties can be related to changes in the mode resonant frequency and the cavity Q factor with and without epoxy by employing material-cavity perturbation theory.

Table 1 A summary of results on dielectric measurement of epoxy

Methods /Frequency	Temp (°C)	Epoxy	E'	E"	(Ref)
Electrodes	40	828/Versamide 140			(1)
240 Hz 2 MHz		50 phr	5 5 10 2	0 8-1 2	
LF Impedance Analyzer	30	Epon 828/U			(2)
500 KHz		uncured	8 80	0 46	
500 KHz		cured 50 min	4 52	0 38	
5 KHz		cured 50 min	5 60	0 60	
0 1/5 FH?		cured 50 min	6 80	2 00	
500 KHz		cured 200 min	3 15	0 20	
Microelectrometer	20	Epon 828/DDS			(4)
10 KHz		mole ratio 1/3	36 0	3 60	
		mole ratio 1/1	22 0	2 20	
Waveguide	room	Fiberite S2/9134B			(5)
2 45 GHz		uncured	5 21	2 084	
		cured	5 21	2 084	
		Hercules AS/3501-6			
		uncured	33 0	1758 9	
		cured	14 5	1099 1	
Transmission lines		Epon 828/T-403			(6)
1 0 2 5 GHz	23	uncured	3 456	0 0044	
	23	cured	3 548	0 0036	
	60	uncured	3 914	0 0102	
	70	uncured	4 013	0 0107	
		Epon 828/Z			
	23	uncured	4 057	0.0106	
	60	uncured	4 686	0 0210	
	70	uncured	4 819	0 0244	

EXPERIMENT

Apparatus

The experimental system for microwave diagnosis and processing is shown in Fig. 1. The microwave energy source is an HP8350C sweep oscillator connected by a HP 11869A adapter with a 1.7 - 4.3 GHz HP 86235A RF plug in. The source incorporates a Varian TWT amplifier which can amplify the signal from 0 to 15 W. An isolator is used to protect the energy source. Two 20 db directional couplers are used to decouple the incident signal and the reflected signal. The reflected signal is rectified by a crystal detector and displayed on an X-Y oscilloscope. The oscilloscope is used to display the resonance absorption curve which is to determine the resonant frequency and the Q factor of the critically coupled cavity.

A cylindrical cavity with a sliding short and coupling probe was mechanically tuned to critically couple in the TM_{012} mode at 3.2 GHz. A diagram of the cavity and sample holder is shown in Fig. 2. A cylindrical teflon holder was filled with the epoxy-amine mixture. The teflon holder was hung in the center of the cavity by a nylon thread. The dimension of the teflon holder is 6.35 cm in length with 0.95 cm I.D. and 0.16 cm thickness. Several advantages for using teflon as a sample holder are very low dielectric loss factor, temperature-independent dielectric properties, high temperature resistance (up to 260° C), and chemical inertness to reactants and products. The cavity with the empty teflon holder is called an unloaded cavity, while the cavity with the epoxy-filled teflon holder is called a loaded cavity. Q factor and resonant frequency of the unloaded and loaded cavity were continuously measured to determine dielectric properties.

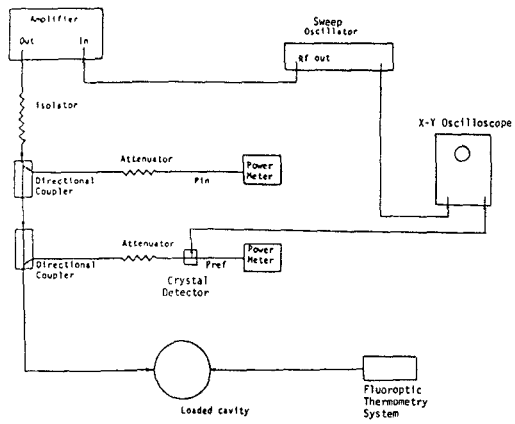

Fig 1 Single Mode Experimental Circuit for Processing and Diagnostic Measurement

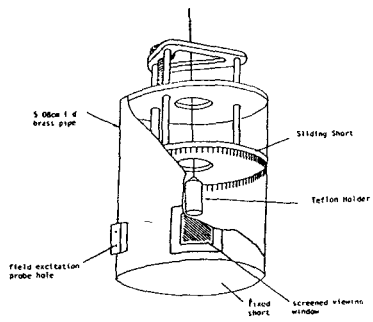

Fig 2 Experimental Cylindrical Cavity

A fluoroptic thermometer (Luxtron Model 750) is used to continuously measure the temperature. A fluoroptic probe is protected by a 3 mm O.D. pyrex capillary tube and placed in the center of the teflon holder.

A differential scanning calorimeter (Du Pont DSC 9300) is used to directly measure extent of cure of epoxy after the epoxy is processed in the single-mode cylindrical cavity.

Materials

The epoxy resin for this study is DER 332 (a low molecular weight DGEBA resin, m.w.=346 g/mole, $CH_2OCHCH_2O\text{-}[C_6H_4C(CH_3)_2C_6H_4OCH_2CHOHCH_2O]_n\text{-}C_6H_4\text{-}C(CH_3)_2C_6H_4\text{-}OCH_2CHOCH_2$), manufactured by Dow Chemical Co.. The epoxy resin is chemically stable before reaction with a curing agent. Diamino-diphenylsulfone (DDS, m.w.=248 g/mole, $H_2N\text{-}C_6H_4\text{-}SO_2\text{-}C_6H_4\text{-}NH_2$) is chosen as a curing agent. Two moles of DER 332 are mixed with one mole of DDS (one equivalent epoxy/one equivalent amine).

Experimental Procedure

The cavity was operated at TM_{012} mode by sweeping frequencies about 3.2 GHz with power input of 3 to 6 W and critically tuned by adjusting the depth of the excitation probe. Before heating, the resonant frequncy and the Q factor of the unloaded cavity were measured using low power levels (12 to 14 mW). Samples of DDS and DER 332 were electromagnetically heated in this resonant cavity using heating times of 10 minutes and 30 minutes. While the loaded cavity was critically tuned to the TM_{012} mode by adjusting sweeping frequency and excitation probe position during the microwave heating process, the resonant frequency, the Q factor, and temperature versus time were measured. After heating was completed, the loaded cavity was switched to be operated at low power level (12 to 14 mW). The resonant frequency, the Q factor, and temperature were still measured during the cooling process. Thereafter, the extents of cure for these two cured mixtures were determined by a differential scanning calorimeter. The dielectric constant and the dielectric loss factor were calculated by changes in the resonant frequency and the Q factor between the loaded and unloaded cavity.

EXPERIMENTAL RESULTS AND DISCUSSION

The temperature, dielectric constant, and dielectric loss factor versus time profiles during microwave curing of epoxy were shown in Fig. 3. The dielectric constant and dielectric loss factor versus temperature profiles during cooling were shown in Fig. 4 and 5. The extent of cure for the mixture was 33.2% for 10 minutes microwave heating and 66.9% for 30 minutes heating.

Temperature rapidly increased from room temperature to 130° C in 10 minutes due to the microwave energy absorption. The temperature continued to rise up to 160° C due to the exothermal reaction, even though absorbed power was already decreasing with decreasing dielectric loss factor after 10 minutes. After the sample had undergone significant reaction, it cooled to a steady-state temperature determined by equilibriation of energy absorption by the sample and convection from the sample to the surroundings.

The dielectric properties of epoxy have been known to decrease with increasing reaction time in an isothermal curing process (4) and to increase with increasing temperature for a specific extent of cure (10). The dielectric properties (E' = 5.4 and E" = 0.323 at room temperature) in this non-isothermal study increased with increasing temperature and reached the maxima (E' = 10.5 and E" = 0.75 at 130° C) in 10 minutes. The extent of

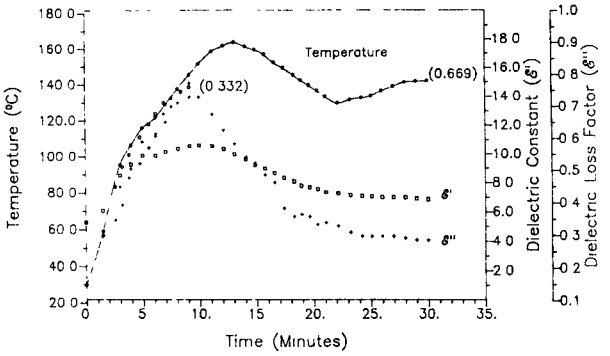

Fig. 3 On-line Temperature and Complex Dielectric Constant versus Microwave Curing Time Profiles in a Sweeping Cavity

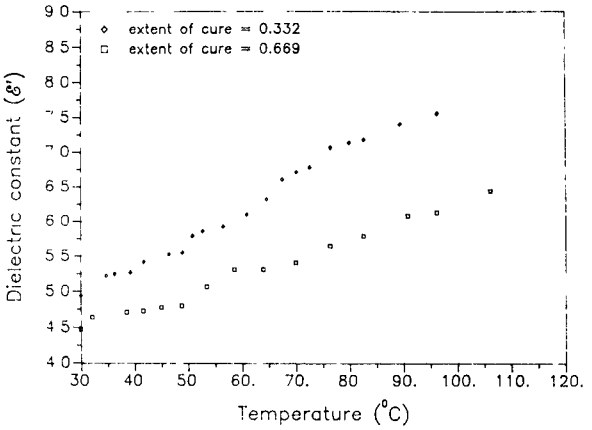

Fig. 4 Dielectric Constant vs Temperature at 3.2 GHz for Different Extents of Cure (Cooling Cure)

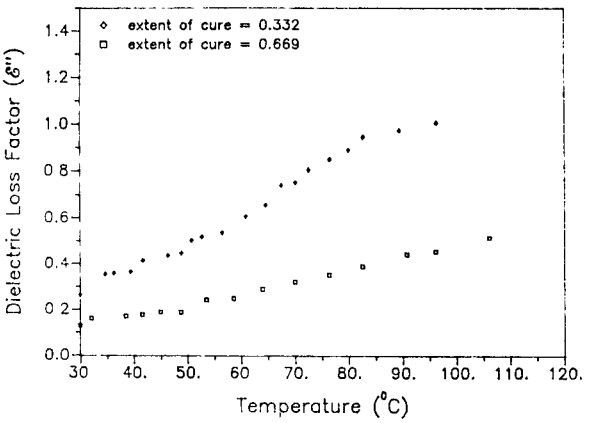

Fig. 5. Dielectric Loss Factor vs Temperature at 3.2 GHz for Different Extents of Cure (Cooling Curve)

cure at these maxima was about 33.2%, which was defined here as a gelation point for this heating cycle. Gelation point is dependent upon viscosity, which depends on extent of cure and temperature for a curing epoxy resin (11). It showed that the dielectric properties below the gelation point were more dependent upon temperature than upon extent of cure during the microwave heating process. The dielectric properties after the gelation point decreased with increasing extent of cure, even though the temperature increased due to the exothermal reaction. It implies that the dielectric properties are more dependent on extent of cure than on temperature after the gelation point during the microwave heating process. The dielectric properties shown in Fig. 4 and 5 decreased with decreasing temperature for a specific cure, and decreased with increasing extent of cure for the same temperature.

CONCLUSION

The dielectric properties of epoxy are functions of extent of cure, temperature, composition, and frequency. This work shows that the dielectric properties of epoxy decrease with increasing extent of cure and with decreasing temperature. It also shows that the dielectric properties are strongly temperature-dependent before the gelation point and strongly extent of cure-dependent after the gelation point.

This work sucessfully demonstrates the use of the microwave sweeping resonant cavity system in conjuction with fluoroptic temperature measurement to process and to on-line monitor the cure of epoxy resins. However, most of the incident power supplied from the sweeping energy source is reflected due to sweeping frequencies. Further research will use a single-frequency resonant cavity to improve power efficiency. It is also required to develop a data base of dielectric properties as functions of temperature and extent of cure in order to properly select microwave heating cycle, and to develop an energy-material balance to interpret and predict the experimental results.

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