Curing Epoxy Resins by Microwave Radiation

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Abstract

Rapid prototyping is a generic process for making rapidly and accurately three-dimensional physical objects of almost any shape. Existing rapid prototyping techniques rely on laser and printing techniques. The use of microwave technology in rapid prototyping has not been explored as yet. In this work, curing process of thin layers of epoxy resins using microwave radiation was investigated as an alternative technique that can be implemented to develop a new rapid prototyping technique. Curing temperature and curing time have been determined for several epoxy mixtures. The mixtures were made up of three commercially available epoxy resins, hardener, aluminium and flydust powder.

The preliminary results showed that the current achievable curing temperature and time required to cure fully the tested mixtures are ~90 ^{o}C and 75 sec. The powder additions did not change significantly the hardening process. It has been confirmed that the curing process is directly correlated to dielectric properties of the material.

Introduction

Most rapid prototyping techniques use the same idea of manufacturing a three dimensional object by building it layer by layer. Using 3-dimensional computer aided design (3D CAD) software an electronic solid model of the object is first developed and then divided into a set of slices to be sequentially built by a relevant rapid prototyping process. In each case the slicing process is adjusted to the rapid prototyping technique to be used as the thickness of the slices and the direction of slicing affect the feature's definition and the manufacturing cost/time of the prototype. Thinner slices give better accuracy, however, the time required for building the prototype is greater and this affects the overall cost. Various Rapid Prototyping developers have developed their own proprietary software to define minimum thickness of the layer and direction of slicing. The minimum thickness of the layer depends also on the viscosity of the material, which has to be considered when mixing with a powder substance. Usually STL files are used for further processing (Jacobs 1996).

Microwave technology can be used as an alternative way for curing layers of material in the rapid prototyping process. It offers the possibility of uniform curing of the epoxy materials by generating instantly heat in the entire part independent of its shape complexity and dimensions. Materials for microwave heating need to be electrically non-conductive and should have a dipole structure. The dipoles are polarised at microwave frequency. When the frequency is high enough the dipoles cannot follow with the reorientation of the electric field and at this point microwave energy is converted into heat. Effective microwave heating is achieved, when the rate of microwave power absorption is greater than the rate of heat dissipation through convection or conduction (Metaxas and Meredith 1983).

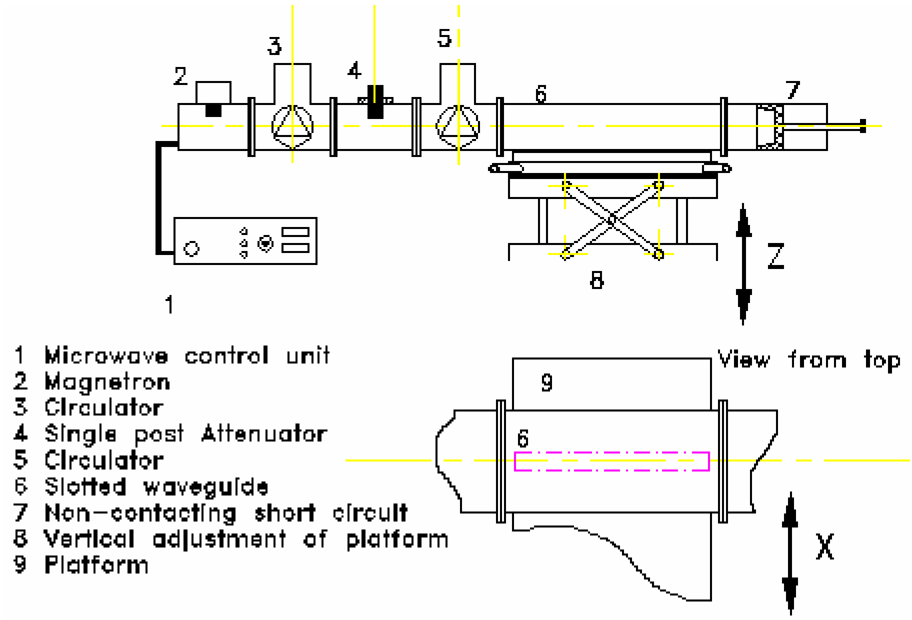

Figure 1: Schematic diagram of the microwave system with the slotted waveguide and short circuit.

Figure 1 shows diagrammatically the experimental set-up for the rapid prototyping process by using the microwave technology, which has been developed, at Queensland University of Technology. The equipment consists of the microwave control unit, Model: GMP 20K/SM which powers the water-cooled magnetron, Model: NL 10250, 2KW 54 REM at 2.45 GHz. The power output is adjustable from 0 to 1.9KW. Via the rectangular waveguide flange WR 340, the magnetron is connected to a circulator, for protection of the magnetron against reflected power coming from the single post attenuator. The second circulator takes care of the reflected power reflected by the short circuit. The WR 340 waveguide system is used as part of the resonance cavity for the dominant TE_{10}-mode, with variable tuning achieved through the short circuit (Lance 1964).

Applying liquid onto the platform a layer of the slice is generated. The liquid is sprayed onto the platform by electrically activated spray-nozzles. The nozzles are aligned across the platform and electronically controlled, to apply the liquid as a thin film to the platform. Using information from the STL-file a contour of a layer is applied. Simultaneously while the platform moves in horizontal direction, the layer passes the slotted waveguide. The slotted waveguide is connected to a 2.45GHz microwave system generating a fringing field of electromagnetic radiation, which penetrates through the epoxy layers on the platform and accelerates the curing process. This process increases the temperature within the epoxy resin and contributes to fast curing. The vertical movement of the platform is equal to the layer thickness, so that the penetration of the fringing field at the slotted waveguide cures each layer uniformly. Depending on settings microwave radiation can propagate deep into the material making sure that the post-curing is not required.

The material of the platform is characterised by its very low dielectric constant so electromagnetic field penetrates easily the platform without generating heat. The microwave that passes the platform is contained by the water-load accommodated beneath.

The goal of this work is to determine the response of existing epoxy systems to microwave treatment in order to assess their suitability for the proposed new rapid

technique. The layer has to be cured quickly to prevent any changes to its form. Nearly instant solidification of the liquid is required to change the liquid into a rubbery form. The thermosetting of the epoxy resin and the microwave heating reapplied for several times in the process of building subsequent layers will advance the curing.

Experimental material

Series of mixtures of epoxy resins with varying amount of hardener (5-40 wt%) and aluminium (0-35wt%, average dielectric loss factor) or flydust (0-35wt%, low dielectric loss factor) powder additions have been tested. There are three reasons for powder additions. Firstly, ability to cure mixtures increases the functionality of prototypes (wider base for material selection). Secondly, the influence of additions with varying dielectric properties on curing process can be examined, and thirdly, the viscosity of the liquid can be controlled. Table 1 shows the compositions of the mixtures used in the present study.

Thin layers of the mixtures of epoxy resins were applied manually onto a glass plate. The thickness of the applied epoxy was varying depending on the composition. The average thickness for each epoxy and mixture type is shown in Table 2.

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Table 1: Composition of mixtures investigated.

FGI R180					Ciba Geigy, LC 3600					Ciba Geigy, GY 9708-1				
Har	Fly	Alu	Temp	Time	Har	Fly	Alu	Temp	Time	Har	Fly	Alu	Temp	Time
wt%	wt%	wt%	^{o}C	sec	wt%	wt%	wt%	^{o}C	sec	wt%	wt%	wt%	^{o}C	sec
0			177	1500	0			180	900 (p)	0			171	600 (nc)
5			165	1080	5			185	960	5			168	540 (b)
10			141	720	10			166	720	10			160	510 (p)
15			137	600	15			154	450	15			115	315 (p)
20			126	390	20			129	435	20			106	270
25			117	360	25			111	240	25			105	240
30			109	300	30			107	135	30			102	210
35			101	270	35			104	105	35			99	180
40			90	210	40			100	75	40			97	150
10	5		143	540	10	5		176	780	10	5		133	360 (p)
15	10		137	390	15	10		145	420	15	10		119	300
20	15		124	360	20	15		135	240	20	15		99	240
25	20		118	330	25	20		134	180	25	20		94	180
30	25		104	240	30	25		108	90	30	25		86	165
35	30		91	210	35	30		107	75	35	30		81	150
40	35		86	180	40	35		106	60	40	35		74	120
10		5	120	360	10		5	161	900	10		5	147	390 (p)
15		10	115	330	15		10	135	390	15		10	106	255
20		15	110	300	20		15	131	300	20		15	103	240
25		20	107	255	25		20	112	150	25		20	94	195
30		25	105	240	30		25	111	105	30		25	92	180
35		30	100	210	35		30	98	105	35		30	85	150
40		35	86	165	40		35	92	75	40		35	82	135

Legend:

Har – hardener
Fly – flydust
Alu – aluminium

Temp –curing temperature
Time – curing time
(b) – mixture overheated, burnt

(nc) – not cured
(p) partially cured

Table 2: Average thickness of epoxy resin layer applied on microscope-glasslide.

	Fgi R 180	LC 3600	GY 9708-1
with hardener only	0.06	0.08	0.47

with hardener & flydust	0.21	0.19	0.43
with hardener & aluminium	0.58	0.13	0.47

Note: Applying the epoxy resin to the glasslide was done manually.

The specimens were cured in a commercial microwave oven, Menumaster, Model 3100 at 1.5KW power. Microwave ovens usually have very complex wave propagation of electromagnetic fields in their cavity. To ensure uniform radiation the specimens were placed in the centre of the power concentration, which has been determined experimentally.

The temperature of the specimen as a function of exposure time to microwave field, and the time taken to cure the specimens were determined by placing an epoxy sample in the microwave oven. The measurements were taken in 60-second intervals. Every 60 seconds the power was turned off and the temperature of the specimen was measured using type K-thermocouple. At the same time the specimen was checked if it is cured by touching with a sharp needle. The specimen was tested for curing through putting light pressure on the surface of the layer. The results are shown in Table 1 and are summarised graphically in Figures 2.

The dielectric constants define the interaction mechanisms of electro magnetic fields with the materials. These interactions depend on the frequency of electromagnetic field and temperature (Sutton et al.1994). Since the dielectric constant determines the ability to absorb microwave energy (Von Hippel 1995), dielectric constant for each of the epoxies tested has been determined by using a Network analyser, HP 8510C, connected to a high temperature dielectric probe HP 85070B (Hewlett Packard 1991).
The measurements were performed at different temperatures. The epoxy resin samples were heated using a temperature controlled auxiliary heater. The results of measurement of dielectric constants are given in Table 3 and 4.

Table 3: Dielectric constant e'[1] and dielectric loss e"[2] measured at 2.45 GHz.

Epoxy	Ciba Geigy GY 9807-1		LC-3600		fgi R180	
Temp [°C]	e'	e"	e'	e"	e'	e"
23			4.1763	0.8566		
25	3.7166	0.4295				
30					4.1981	0.8217
40	3.7486	0.4416	4.6446	1.1492	4.6125	1.0802
60	4.1604	0.7306	5.0041	1.2722		
80	4.3781	0.8697	5.3267	1.3364	5.3012	1.3294

[1] Dielectric constant (e') characterises the penetration of microwaves into the material.
[2] Dielectric loss (e'') indicates the material's ability to dissipate energy.

Table 4: Dielectric constant e' and dielectric loss e'' measured at 2.45GHz and 40%wt hardener.

Epoxy	Ciba Geigy GY 9807-1		LC-3600		fgi R180	
Temp [℃]	e'	e"	e'	e"	e'	e"
26			0.9861	0.0005		
27	4.3450	0.7666				
30					4.4047	0.8948
40	4.4815	0.8359	4.3168	0.9744	4.2665	0.9122
60	4.6117	0.9646	5.2068	1.3165		
80	4.5214	0.9573	5.1557	1.2414	3.9052	0.3931

Results and Discussion

The results of the measurements have been summarised graphically. The curing temperature and curing time are presented as a function of chemical composition of the mixture (see Figure 2).

Generally, the curing time and the curing temperature are decreasing with the increase of hardener and powder additions (Figure 2). It appears that using LC 3600 resin lower curing temperature and shorter curing time can be achieved. Low curing temperature helps to avoid distortion in the final product. Short curing time is necessary to avoid deformation of the liquid layer, which can flow on the surface. This also depends on viscosity of the mixture.

It is apparent that in all cases the curing temperature and curing time depend almost exclusively on the concentration of the hardener. This is especially evident in the case of LC 3600 resin with one exception where Al additions change significantly the FGI R180 epoxy behaviour. However, not to the desirable extent. The powder additions only marginally change these characteristics.

The measurements of the dielectric constants have been conducted at the frequencies from 1.0GHz to 20.0GHz (broad-bands) to determine the relaxation frequency as shown in Figure 3. Following the broad-band investigation (measurement is established over a wide range of frequencies), there were also dielectric test performed at a narrow-band, frequencies from at 2.2GHz to 2.55 GHz as shown in Figure 4.

The broad band measurement from at 1.0GHz indicates a slight decrease of the dielectric constant (e') and the dielectric loss (e''). Over a wide range of frequencies, the dielectric property does not change significantly until the relaxation frequency at around 17GHz.

At this frequency the microwave treatment would be the most effective. However, the operational frequency of the equipment available is 2.45GHz, where the dielectric loss (e'') has a value of about 0.9 for epoxy resin Ciba Geigy, LC 3600 at 23℃, as shown in Table 3, and also on Figure 4.

As it can be seen the dielectric constant and dielectric loss factor do not vary in the range of 2.2 to 2.55 GHz frequency. Table 3 and 4 show that LC 3600 resin has larger e' and e" constants. Especially, the dielectric loss factor is significantly larger. Considering the curing temperature and curing time with respect to these two constants it appears that a correlation exist. The curing temperature is proportional to e" and the curing time reciprocally proportional (see Table 5, which is formed by extraction of the data from Tables 1, 3 and 4). The good performance of the LC 3600 resin can be attributed to its dielectric properties.

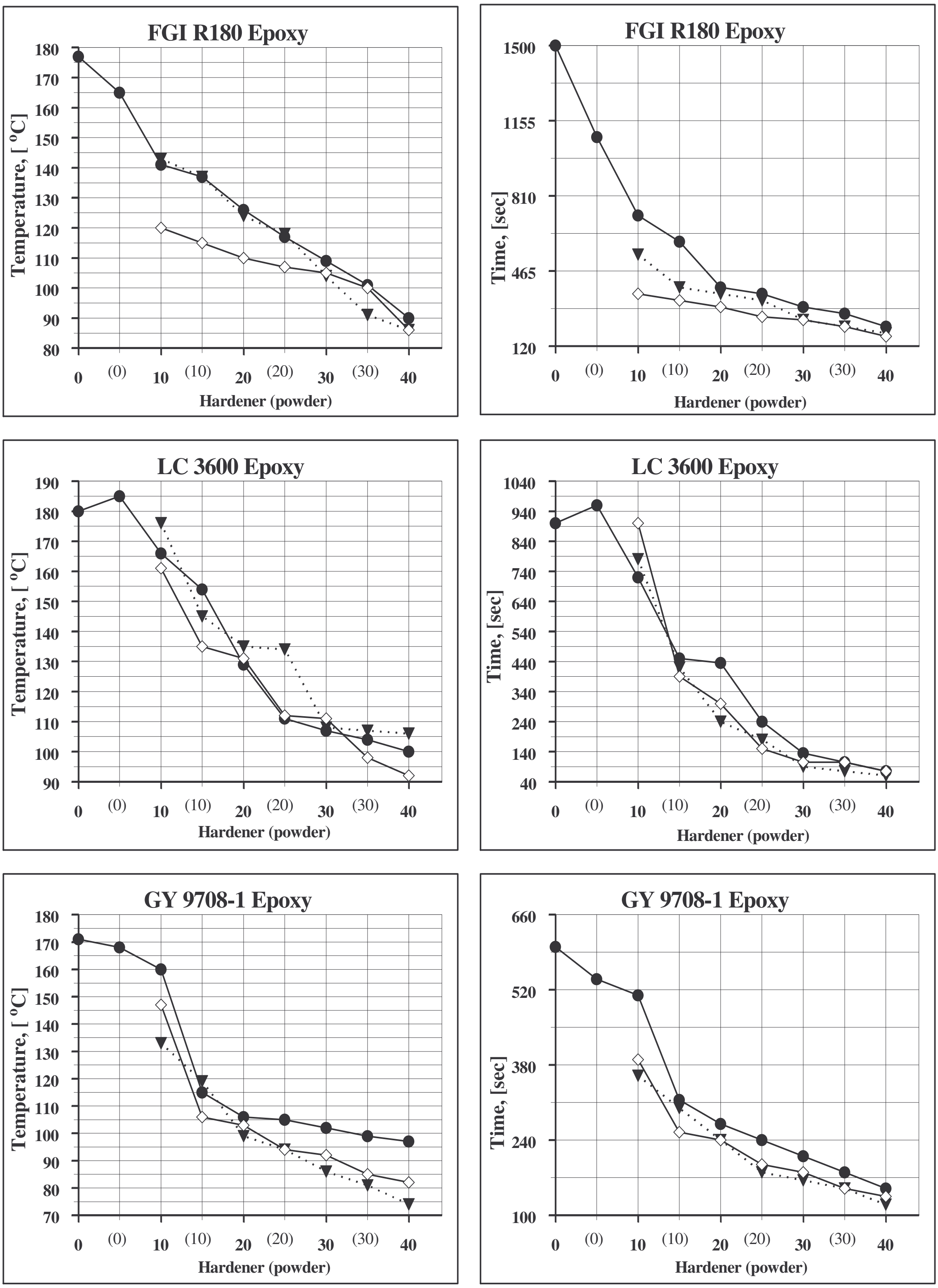
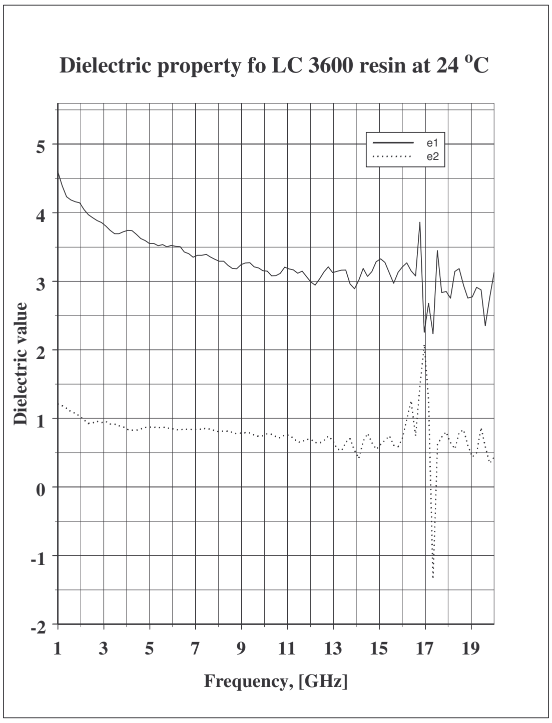


Figure 2: Curing temperature and time as a function of the composition of the mixtures.

● - epoxy with hardener

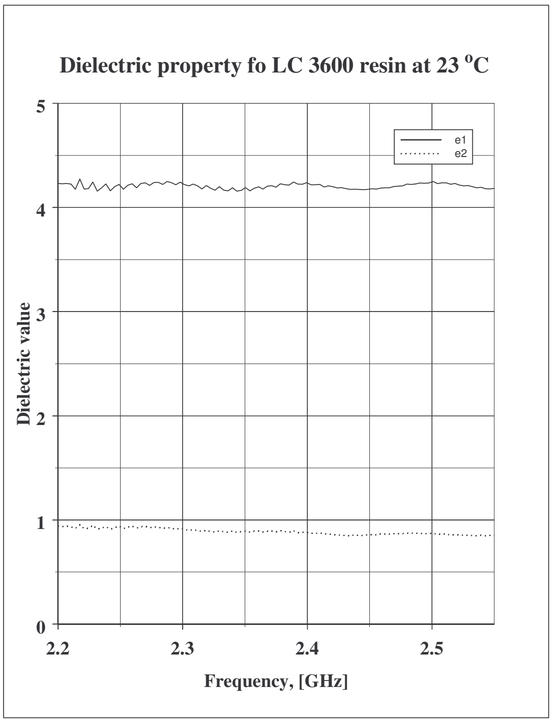
▼ - epoxy with hardener and flydust powder (content in parentheses)

✧ - epoxy with hardener and aluminum powder (content in parentheses)



(e1 = e' ; e2 = e'')

Figure 3: Shows the value of the dielectric property of epoxy resin Ciba Geigy LC3600 at 1.0 GHz to 20.0 GHz (broad band).



(e1 = e' ; e2 = e'')

Figure 4: Shows the value of the dielectric property of epoxy resin Ciba Geigy LC 3600 at 2.2 GHz to 2.55 GHz (narrow band).

Table 5: Correlation between parameters tested and dielectric properties of the resins.

Epoxy	Curing Temp.	e'	e"	Curing Time
LC 3600	100	5.2	1.25	70
GY 9708-1	97	4.5	0.96	150
FGI R180	90	3.9	0.40	210

Conclusions

Mainly hardener content controls the curing time and curing temperature. The powder additions influence them only marginally.

The best results are achieved for the LC3600 epoxy resin. The curing temperature is about 90 ^{o}C, and curing time is about 75 seconds. Our aim now is to achieve a rubbery state. This will be a part of further investigations.

A direct correlation between the dielectric properties and epoxy performance has been confirmed. Based on these results a new set of experiments will be designed to determine relationships between dielectric constants, mixture composition, and temperature.

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