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Indian
Journal of Advances in
Chemical Science

Indian Journal of Advances in Chemical Science S1 (2016) 248-252

Microwave Assisted Processing of Polymer Matrix Composites: A Rapid and Energy-efficient Alternative

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Received 1th April 2016 ; Revised 16rd May 2016; Accepted 16th June 2016

ABSTRACT
For polymer composite product manufacture, curing is the most critical step in achieving desired mechanical properties. Conventional cure processes involve thermal curing in ovens and autoclaves where the process is time and energy intensive. Microwave assisted curing is one of the proven methods of curing polymer composites that could lead to substantial reduction in cure cycle time, energy requirements, and operational costs due to its instantaneous, volumetric mode of heating. Our results on microwave processing of aerospace grade glass-epoxy composites have shown that the process time saved is ~90% and energy saved is ~60% vis-à-vis a conventional thermal curing process. In addition, the cure uniformity, thermal and mechanical properties achieved by microwave processing are comparable/superior. Thus, an alternative cure approach has been developed at CSIR-NAL for the first time in India, which has better techno-economic significance for aerospace composites. The efficacy, scalability, and versatility of molecular weight assisted curing have been realized from chemistry to component level through our unique microwave cure facility and comprehensive studies therein. This article is mainly centered on the challenges and successes of microwave assisted processing of composites for structural applications. Proposed futuristic directions are also outlined.

Key words: *Microwave, Curing, Rapid, Energy-efficient, Polymer matrix composites.*

1. INTRODUCTION

Microwave processing is well known and is most popular in the food processing industry. It is evident from the huge number of models of microwave ovens hitting the market since the past two decades. However, the microwave is yet to penetrate the composites processing sector in a big way. The reasons for this are many. First and foremost is the level of understanding of the microwave - materials interactions. Other possible factors are inability to achieve uniform heating of the substrate which is evident from the hot-spots present on the surface; low repeatability and reliability; difficulties in scaling up of the process; limited penetration depths, etc.

A survey of microwave research in India suggests that microwave curing has been done at several institutes mainly out of academic interests. Coupon level tests have been done to characterize the specimens. Moreover, the equipment used is also mostly popular domestic microwave ovens with slight modifications, if at all. Furthermore, microwave ovens have been extensively used for the synthesis of organic chemicals due to the benefits of solvent-less synthesis as well as rapid preparation. Microwave food processing is rapidly gaining popularity in India. However, microwave curing of polymer composites is still an emerging area.

Polymer composites are increasing replacing metals and ceramics for a diverse range of applications from aerospace to automobile, food processing to chemical processing, consumer goods to medical instruments, and the list continues to grow.

This is mainly due to innovations in polymeric materials which are lighter-in-weight, possess high specific strength, impact resistant, corrosion resistant, and structurally durable when converted into reinforced composites.

Curing is the most important phase of composites processing leading to product manufacture. The conventional cure processes involve thermal curing in hot air ovens and autoclaves where the cure process is time and energy intensive (Table 1). Microwave

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assisted curing is one of the alternative, proven methods of curing polymer matrix composites (PMCs) that could lead to substantial reduction in cure cycle time, energy requirements, and operational costs due to its volumetric mode of heating (Figure 1). In the present scenario of energy crunch looming large in the product manufacturing sector, it is extremely important to embrace non-conventional technologies that are both time and energy-efficient.

In this context, with the aim of faster and energy-efficient curing of aerospace composite parts, a unique microwave cure facility has been setup for the first time in the country at CSIR-NAL [1].

2. THEORETICAL BASIS

The fundamental as well as the most preferred mechanism of microwave heating involves agitation of polymer molecules or ions that oscillate under the effect of an oscillating electric or magnetic field, producing heat as a result of dipolar polarization depicted in Figure 2.

During Dipolar polarization, owing to intermolecular forces, molecules experience inertia and are unable to follow the field. Thus, frictional heat is generated.

The two basic parameters governing the microwave-materials interactions are the complex dielectric constant ε* and the loss tangent, tan δ, as defined by

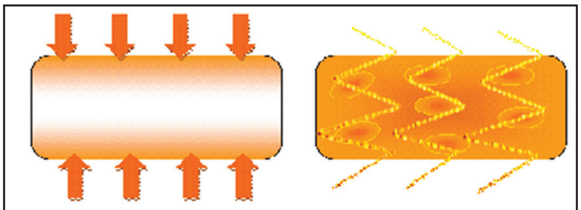

Figure 1: Heat transfer phenomenon: Thermal cure versus microwave cure.

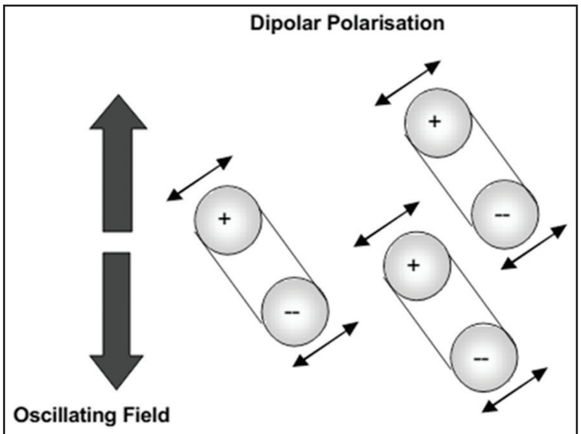

Figure 2: Mechanism of microwave heating.

the following equations:

$$\varepsilon^* = \varepsilon' - i\,\varepsilon'' \quad (1)$$

$$\tan\delta = \varepsilon''/\varepsilon' \quad (2)$$

The dielectric constant (permittivity), ε', defines the ability of a molecule to be polarized by the electric field and to store electric charges. The dielectric loss factor, ε″, is a measure of the amount of microwave energy lost to the sample by heat dissipation. The "lossyness" of dielectric materials at a given frequency and temperature is defined as the loss tangent.

The exact dependence of the heating rate upon the presence of a dielectric field is given by the dielectric heating equation.

$$p = 2\pi f\, \varepsilon_0\, \varepsilon'' E_i^2 \quad (3)$$

Where p = Power dissipation density, f = Frequency, ε_0 = Permittivity of free space, ε" = Dielectric loss factor and E_i = Electric field intensity.

The dielectric heating equation is the basis for deciding the best frequency that can be employed for a specific application of microwave heating.

Most of the available commercial microwave ovens are designed to operate at 2450 MHz (λ = 12.25 cm and energy = 1.02×10^{-5} eV).

3. MICROWAVE ASSISTED PROCESSING OF POLYMER COMPOSITES

Although the first documented utility of microwave heating for vulcanization of rubber dates back to 1969 [2], research publications began to appear from the 1980s. With more insight and understanding, researchers across the world started studying various facets of microwave cure, resulting in an exponential rise in the number of publications and patents. Some of the most significant research findings are reported below. The research areas focused upon include:

3.1. Type of Microwave Applicator

Waveguides, single mode, multimode, traveling wave tubes, variable frequency type, etc., [3-7]. Some of the researchers used domestic microwave ovens too [8]. However, based on our extensive experiments [9], it was found essential to use custom-designed molecular weight (MW) chambers for uniform curing of glass-epoxy PMCs [10-13].

3.2. Sample Sizes

Mijovic and Wijaya [14] carried out comparative calorimetric measurements of an epoxy cured in a small, single mode microwave oven at 2.45 GHz and by thermal cure. They compared the degree of cure and the glass transition temperature (Tg) of samples cured isothermally in both the modes. They were the first to report that at a given isothermal temperature, cure proceeded slightly faster in thermal than in the microwave fields. The glass transition range was broader or appeared as a two-step glass transition in the microwave cured samples, on curing of larger composites, researchers from University of Delaware [15] suggested MW process as an alternative to autoclave cure for thick composites. They used a large, cylindrical (4 ft. length, 2½ ft. diameter), multimode cavity at 2.45 GHz.

3.3. Type of Resins and Reinforcements

Nightingale and Day [8] investigated two epoxy systems with different dielectric loss factors toughened with polyetherimide (PEI) reinforced with UD carbon prepregs. The composites were then cured in three modes: Autoclave, partial autoclave + microwave, and complete microwave curing. It was reported that autoclave cured System 1 had greater flexural strength and interlaminar shear strength (ILSS) than System 2. For the microwave post-cured composites, system 2 showed better strength and modulus. The strength of fully microwave cured systems 1 and 2 composites was similar but was influenced by the structure of PEI and void content. Further, the mechanical properties of the fully microwave cured composites were better than those of the microwave post-cured composites. Hosur et al. [16] studied the microwave curing of nanophased epoxy that resulted in considerable reduction in processing time without compromising the properties. In studies by Gourdenne et al. [5,17], the effect of fillers upon dielectric properties of polymers or composites, using Cu, Al, C-black, or other conducting materials has been carried out. Carbon fibers have been studied as coabsorbent materials in the MW cure of epoxy composites. The specimens showed higher interfacial shear strength than thermally cured composites. Similar studies were reported for bismaleimide [18], polyimide (RP-46), Glass-Graphite-RP-46 composites [19], epoxy-anhydride [20], isocyanate-epoxy [21], etc.

3.4. Temperature Measurement Techniques

One major hurdle in MW processing is the difficulty of *in situ* temperature measurements. Conventional thermocouples are not suitable since they can cause arcing and might damage the MW source. Researchers have tried to circumvent this problem through the use of embedded thermocouples, shielded thermocouples, optical fiber probes, and non-contact infrared pyrometers [22]. However, the optical techniques assume the emissivity of the sample, which may lead to erroneous results. These limitations have led us to believe that application of infrared thermography (thermal imaging) might give very valuable insights on the temperature distribution profile of the curing substrate online.

4. MICROWAVE CURE HIGHLIGHTS AT CSIR-NAL

At CSIR-NAL, under different programs, a full-fledged microwave cure facility was established through extensive & systematic research studies undertaken in a phased manner during 1999-2008, starting with a domestic oven to a hybrid heating oven till date, as shown in Figure 3.

4.1. Conveyor MW System

After coupon level studies in a domestic and lab-scale oven, scale-up of the process was realized in a conveyor-type MW facility from flat laminate level to representative components level for aerospace applications by curing a nose random of an advanced aircraft. Its profile being both thick and curved provided a good choice for these studies. Recently, different thickness glass fiber reinforced polymer (GFRP) composites as well as Carbon FRP composites were successfully cured using vacuum assisted microwave

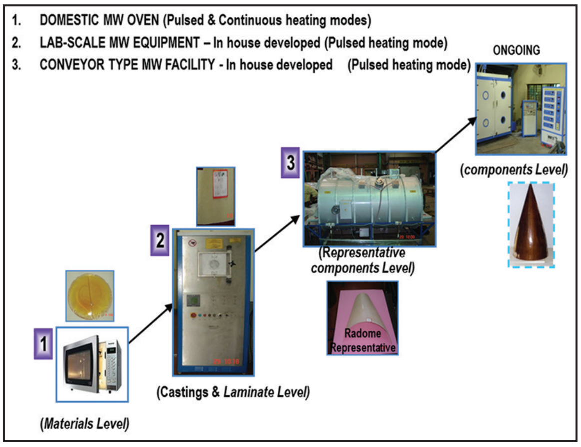

Figure 3: Emergence of microwave cure at NAL.

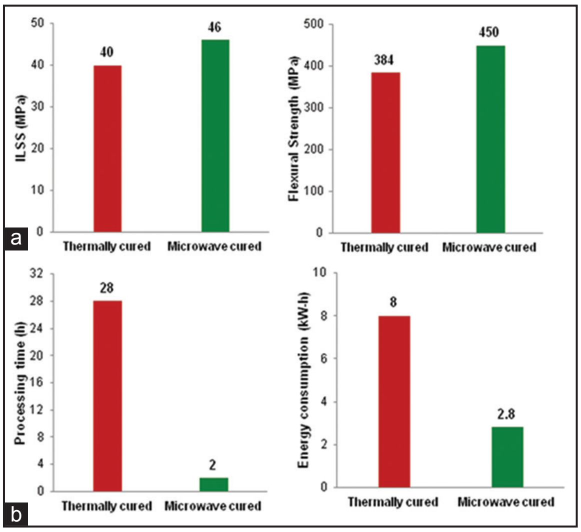

Figure 4: Thermally cured versus microwave-cured glass fiber reinforced polymer, (a) mechanical property (b) time and energy consumption comparison.

Table 1: Thermal cure versus microwave cure.

Thermal cure	Microwave cure
Cure cycle - Order of hours	Cure cycle - Order of minutes
Use of expensive electrical energy	Very low energy inputs
Prone to frequent operational/maintenance complexities	Clean and less prone to operational/maintenance complexities
Typically very large shop-floor areas	Shop floor area limited to fabrication machinery only
Very high equipment costs	Equipment costs relatively low
Cure cycle - order of hours	Cure cycle - Order of minutes
Use of expensive electrical energy	Very low energy inputs

Table 2: Mechanical properties of MW cured GFRP composites.

Laminate thickness (mm)	ILSS (MPa)		Flexural strength (MPa)	
	THC	MWC	THC	MWC
2	38	40	361	350
3	40	46	410	450.1
6	36	43.5	450	521.1
9		35.6		337.6

GFRP=Glass fiber reinforced polymer, ILSS=Interlaminar shear strength, MW=Molecular weight, THC=Thick hybrid composites, MWC=Maximum water content

curing employing in-house developed dielectric molds that resulted in fast and energy-efficient cure without compromising on thermal/mechanical properties (Figure 4a and b).

The Tgs of different thickness laminates subjected to MW curing were in the range of 110-115°C - equivalent to thermally cured Tg. The ILSS and flexural strength values of both thermally cured and microwave cured GFRP are presented in Table 2. It is evident from the Table 2 that the mechanical properties of MW-cured GFRP are superior even with increasing thicknesses.

4.2. Component Level MW Cure

Microwave curing of a conical composite component using dielectric tooling was done (Figure 5) inside the conveyor-type MW facility. Epoxy impregnated glass layers were utilized for fabrication. The quality of cure and the temperature uniformity of the component were monitored using FLIR thermal imaging camera. The MW process was 88% faster and 70% more energy-efficient as compared to thermal curing. The

Figure 5: Thermal and actual images of molecular weight cured conical component.

cured conical component was characterized by Tg measurements and non-destructive tests.

5. CONCLUSIONS

At CSIR-NAL, the efficacy, scalability, and versatility of MW assisted curing in comparison with conventional composite cure techniques for aerospace have been realized through our unique microwave cure facility setup and comprehensive R & D studies. Benefits of MW curing from coupon to component level have been demonstrated. Now, there is a need for transfer of this technology to the societal needs such as small & medium scale industries by evolving customized solutions.

6. ACKNOWLEDGMENTS

The work is a result of teamwork and various in-house & sponsored projects. The author thanks all the team members at CSMST-FRP and the sponsors. Special thanks to Dr. RMVGK Rao & Professor Krupashankara, who envisioned and were catalytic in bringing this work into some shape.

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***Bibliographical Sketch**

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