MICROWAVE CURING OF LONG FIBER REINFORCED COMPOSITES IN AN OPEN ANTENNA SYSTEM

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Abstract.
In the present work, microwave radiation has been employed in order to polymerize the resin of long fibre reinforced composites[1]. A magnetron of 2000W and an open antenna system inside an isolated cabin of 8 meters long and 4 meters width have been used for microwave curing in the infusion process. The research includes the determination of the dielectric function of the resin and the assessment on microwave susceptors suitable to enhance the curing time. Process parameters were also studied and compared to the traditional heating process. A cost effective method for high size composites manufacturing was achieved.

1 Introduction

Long fiber reinforced composites (LFRC) are nowadays widely employed for the development of low weight and high performance products in several applications in a competitive manner. These properties make composites suitable for the replacement of traditional materials (metals or wood) mainly in the transport (airplanes, cars, trains, trucks, passenger buses) renewable energy (windmill blades) and construction and edification (swimming pools, piping, facades, pultruded structures) sectors.
As a general rule, for the manufacturing of a LFRC two stages are needed: first a thermoset resin impregnates a preform, which is a textile in the form of a woven or non-woven reinforcement with a specific shape corresponding to the final part. After this, the resin polymerizes and it yields to a solid piece. Depending of factors such as the specific components of the LFRC, the number of parts produced, the tolerance on their dimensions and the level of defects allowable, a specific approach is employed. It goes from a simple *hand lay up* to a high performance *autoclave* processing. The most time consuming step in LFRC manufacturing is usually the polymerization of the resin[2]. In order to reduce the whole cycle and improve the competitiveness of the process, polymerization kinetics is enhanced by increasing the temperature of the sample. Traditional heating mechanism in LFRC is heat conduction: by means of a heated mould or a chamber at controlled temperature or oven it is possible to heat the uncured resin and increase the polymerization resulting in the reduction of the cycle time. Temperature is increased through the thickness of the composite under a determined profile, which means that the higher temperature corresponds to the surface in contact with the heated mould. A thin composite will be relatively quickly heated while a thick one will require more time. In addition, this approach requires an excess of energy

consumption because the temperature of the mould or oven has to be increased before the heat is conducted towards the composite.

Microwave technology might be used for resin heating purposes with a major change in the overall mechanism. Microwave radiation generates heating within the material rather than relying on heat transfer through conduction and convection. It is more appropriate to consider microwave heating as conversion of electromagnetic energy to thermal energy rather than heat transfer[3] In addition, microwave processing offers several advantages over the conventional thermal processing methods, including rapid, selective and volumetric heating[4], energy savings, reduced processing time[5] and improved processing control[6]. It has also been described that mechanical properties of microwave cured composites are improved when they are compared to composites manufactured by traditional heating methods. In this sense, interlaminar shear strength (ILSS) of carbon reinforced epoxy composites are 9% higher[7] after microwave curing, probably due to a lowering of resin viscosity in the initial stage of the curing process.

The heating characteristics of a particular material under microwave irradiation conditions are dependent on its dielectric properties. The electric nature of dielectric materials can be described by their dielectric function, which described the interaction of electromagnetic fields with materials, and therefore determine the behavior of the materials in electromagnetic fields[8]. The dielectric properties determine how rapidly the material will heat in heating with microwaves. More detailed discussions and definitions are available in any number of good references, among which the following have been particularly useful to the author [9, 10]. Most dielectric materials are nonmagnetic, so their magnetic permeability has the same value as $\mu_o = 4\pi\ 10^{-7}\ \frac{Vs}{Am}$. These materials, however, have permittivities different from that of free space. The permittivity can be represented as a complex quantity (1),

$$\varepsilon=\varepsilon'-j\varepsilon'' \tag{1}$$

where $j = \sqrt{-1}$. The complex permittivity relative to free space is then given as (2)

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} = \varepsilon_r' - j\,\varepsilon_r'' \tag{2}$$

where $\varepsilon_o = 8.85\ 10^{-12}\ \frac{As}{Vm}$ is the permittivity of free space, the real part ε'_r is called the dielectric constant and the imaginary part ε''_r is the dielectric loss factor. These two quantities are the dielectric properties of practical interest for heating and called the dielectric function of a material. The dielectric constant ε' is associated with the ability of a material to store energy in the electric field in the material, and the loss factor ε'' is associated with the ability of the material to absorb or dissipate energy, that is, to convert electric energy into heat energy. The dielectric loss factor, for example, is an index of the tendency of materials to warm up in a microwave oven. The dielectric constant is also important because of its influence on the distribution of electric fields. The dielectric function is a function of temperature and frequency.

In addition to the above mentioned thermal/kinetic effects, microwave effects that are caused by the uniqueness of the microwave dielectric heating mechanisms must also be considered. These effects should be termed *specific microwave effects*[11] and shall be defined as accelerations that can not be achieved or duplicated by conventional heating, but essentially are still thermal effects. In this category fall, for example 1) the superheating effect of solvents at atmospheric pressure[12], 2) the selective heating of, for example, strongly microwave absorbing heterogeneous catalysts or reagents in a less polar reaction medium[13, 14,15], 3) the formation of *molecular radiators* by direct coupling of microwave energy to specific reagents in homogeneous solutions (microscopic hotspots)[16] and 4) the elimination of wall effects caused by inverted temperature gradients. Microwave effects are the subject of considerable current debate and controversy [17].

Although the important advantages of the microwave approach for curing composites, it has several drawbacks, mainly focused on the availability of industrial equipment to do so. Microwave ovens (even those specially designed for microwave curing of high size composites) are not able to produce a homogeneous electromagnetic field over the part. The main consequence is that hot spots are produced in the sample. It includes modern multimode microwave ovens, those which include a mode stirrer. However, in the present work the main drawback is solved by employing an open antenna system. By means of such set up, a portal crane or robot is able to conveniently move the antenna over the surface of the sample, avoiding hot spots and permitting the selection of the best curing strategy.

2. Experimental.

In the present work, a specific open antenna system has been designed and implemented for the curing of glass reinforced polyester composites. In order to take advantage of this technology, a proper determination of the dielectric function of the resin, a selection of suitable microwave susceptors and the simulation of the electromagnetic field generated by a cylindrical antenna have been carried out. A 3D shape composite, corresponding to a section of a boat hulk, has been microwave polymerized after an infusion process. Thermographic and calorimetric analyses have been employed to demonstrate the complete curing of the polyester resin within a reduced cycle time.

2.1. Materials.

The resin system studied in the present work is an ortophtalic polyester resin (Polres 509 from Gazechim). Several microwave susceptors have been considered, mainly conductive fibers, metal fillers, dipolar organic additives and inorganic additives. E-Glass fiber in the form of a woven textile of 450 g/sqm and the proper catalytic system of OcCo (6%) and Methyl ethyl ketone peroxide have been employed.

2.2. Resonant cavity.

A resonant cavity is used in our work to determine the dielectric function[18,19] of the polymer materials figure 1. The resonant cavity is put out of tune because of the sample inside the resonator. From the frequency shift and the reduction of the quality of the resonance the dielectric function may be calculated.

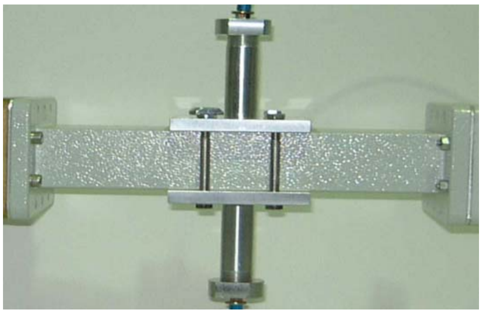

Figure 1.- Microwave resonator

2.3. Differential scanning calorimeter (DSC)

DSC studies were carried out on a *Perkin Elmer DSC 7* to determine the curing degree of samples after its microwave assisted manufacturing. Small size samples (<10 mg) were heated from 20ºC up to 250ºC at 10ºC/min in an inert nitrogen atmosphere. Samples were taken from different locations on each composite panel.

2.4. Open antenna microwave curing system.

A system mainly consisting of a six axis robot and a 2000W magnetron (2.45GHz) was put together with a cylindrical type antenna inside an isolated cell. The dimensions of the cell were 8 meters long, 4 meters width and 4 meters height (figure 2).

Figure 2.- Isolated cell with 6 axis robot and magnetron

2.5. Simulation of the electromagnetic field with the cylindrical antenna

The development of new microwave processes and the dimensioning of the microwave system engineering are so far mainly based on the long-time experience of the microwave companies and institutes. In the last years the possibilities of the numerical simulation of scientific and technical processes have increased enormous with the fast development of the hardware of computers. A common and powerful tool for the determination of the electromagnetic field distribution and the resulting heating in complex geometries with variable shapes and inhomogeneous media is numerical simulation using FEM. For the calculations the software tool *Comsol Multiphysics* was used, which is an advanced, more general software package for numerical modeling and simulation. The solution of Maxwell's equations is supported by an *Electromagnetic Module* with various application modes. The illustration of microwave fields and the resulting heating in combination with temperature dependent material properties facilitate an efficient development of new microwave processes and deepen the theoretical understanding.

For the determination of the electrical field strength the Maxwell Equations have to be solved. The processed product is part of the system and must be regarded with its effect on the system. This is not analytically calculable with exception of only a few examples, but it is numerically calculable. For a harmonically oscillating electric field at 2.45 GHz Maxwell's Equations can be combined to the wave equation (3):

$$\nabla \times \left(\frac{1}{\mu_r} \nabla \times \vec{E}_0 \right) - \varepsilon_0 \mu_0 \omega^2 \left(\varepsilon_r - \frac{i\sigma}{\omega \varepsilon_0} \right) \vec{E}_0 = \vec{0} \qquad (3)$$

where f is the frequency of the electromagnetic field, the angular frequency ω=2π f, and electric conductivity is σ. This equation was solved by Comsol in a region of interest which is bordered by some simple boundaries. For more qualitative studies metallic surfaces can be considered as perfect electric conducting.

Microwave excitation was performed by a feeding structure with a well-known mode, the appropriate matched boundary condition (4) eliminates all waves with the specified propagation constant β:

$$\vec{n}\times(\nabla\times\vec{E})-i\beta\vec{n}\times(\vec{E}\times\vec{n})=-2i\beta\vec{n}\times(\vec{E}_0\times\vec{n}) \quad (4)$$

Further useful boundaries in the package like e.g. a low reflecting boundary for open ends of metallic structures can be gleaned in.
In the figure 3, the set-up is shown in principle. This set-up was identical with the real set-up. The resin was lying over a non microwave absorbent mould and completed by a metal sheet. The distance between the metal sheet and the middle of sample had to be an odd integer multiple of the wave length inside the material.

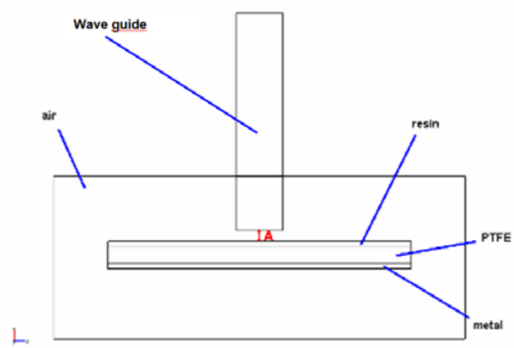

Figure 3.- Set-up of the microwave antenna above the sample

3. Results

According to the previous introduction and after a vast research it was decided to select microwave absorbers that might be catalogued in the following groups:

Conductive fibers
Carbon and metal fibers are included in this group. The former were the only ones tested in this work because it was thought that the behavior of metals against the microwave radiation could be better studied selecting some metals and metal oxides than metal fibers. Moreover, this filler exert and additional reinforcement effect. Carbon fibers have a relatively high resistivity and therefore heat the surrounding matrix very effectively. The thermal profile has a maximum at the surface of the fibers.

Metal fillers
Metal fillers can be as well classified as metals, metal oxides and ferroelectric fillers. All of them are characterized by an inherently strong capacity of electromagnetic energy dissipation at microwave frequencies. The presence of these inclusions, especially if they are conductive (most of the metal fillers), can strongly influence the way in which the resin interacts with the microwave radiation. Conductors also modify the electric-field pattern in and around the resin, potentially resulting in very different heating profiles than with the neat resin. The effect of these conductive additives on microwave heating depends on the size, shape, concentration and electrical resistivity of the inclusions and their distribution in the matrix.

Dipolar organic additives

Microwaves are not directly interactive to a high number of resins. For this reason the addition of fillers with absorbing groups is desirable. Microwave absorbing functional groups are epoxy, amine, cyanate (and isocyanate), hydroxyl, sulfonamides, phthalates, because all of them form strong dipoles. As the principal mechanism of microwave absorption in a polymer is the reorientation of dipoles in the imposed electric field, the presence of these groups in the molecule is necessary. The materials with the greatest dipole mobilities will exhibit the most efficient coupling. The efficiency of this coupling is dependent on the dipole strength, its mobility and mass, and the matrix state of the dipole. Highly dipolar organic additives suitable for this application are aromatic sulphonamides, alkyl phthalates, alkanol amine carboxylates, polyoxyethylene glycols and related ethers and esters

Inorganic and transparent additives

When the additives are inorganic and transparent to microwaves, such as glass fibers and silica powders, the electromagnetic beam is scattered when it goes through the fillers because of a gradient of optical index between the mineral and organic components. Therefore this effect can modify the heating profile[20]. Although our objective is to find a suitable absorber filler it was decided to ad some transparent additives in order to study their effects. Glass fibers are obviously included in our composite, so it was thought that the addition of silica gel would be interesting.

Tests were done with a polyester resin (Polres 509) without functional groups able to specially interact to the electromagnetic field generated for the cylindrical antenna, in order to evaluate the different additives above described. Results are shown in table 1.

Sample	**Additive group**	**Time exothermic peak (seconds)**	**Disadvantages**
PRO04-0263-01-00	Metal filler 1	500	----
PRO04-0263-01-03	Metal filler 2	400	Colour change Difficult dissolution Cracking
PRO04-0263-01-04	Metal filler 3	407	Colour change
PRO04-0263-01-05	Metal filler 4	420	Burn at this power
PRO04-0263-01-06	Metal filler 5	450	Colour change
PRO04-0263-01-07	Metal filler 6	567	Colour change Cracking
PRO04-0263-01-08	Metal filler 7	340	Colour change Difficult dissolution Cracking
PRO04-0263-01-09	Metal filler 8	360	Colour change
PRO04-0263-01-10	Dipolar organic	410	------
PRO04-0263-01-13	Dipolar organic	460	------
PRO04-0263-01-14	Dipolar organic	415	Cracking
PRO04-0263-01-15	Transparent additives	435	Burn at this power Cracking
PRO04-0263-01-16	Dipolar organic	293	Cracking
PRO04-0263-01-17	Dipolar organic	447	-----

PRO04-0263-01-18	Dipolar organic	340	Colour change
PRO04-0263-01-19	Dipolar organic	287	-----
PRO04-0263-01-20	Dipolar organic	360	Colour change Difficult dissolution Cracking
PRO04-0263-01-21	Dipolar organic	600	Colour change Cure in recipient before be introduced in the mould

Table 1.- Results of the research with microwave susceptors

The optimum results were obtained with the dipolar organic additives. The dielectric function of the resin modified with several concentrations of several dipolar organic additives was determined by using a *resonator*. The information obtained was employed for the simulation of the electromagnetic field generated by a cylindrical antenna over the sample. Figure 4 shows the heating of the resin as a consequence of the microwave radiation as a function of the distance of the wave guide to the sample. It was obvious that the heat spot were central located under the wave guide, so that the one-to-one correspondence of the heating area to the microwave spot was possible. The distance between the sample and the wave guide was not so critical in the range between 1cm and 5cm.

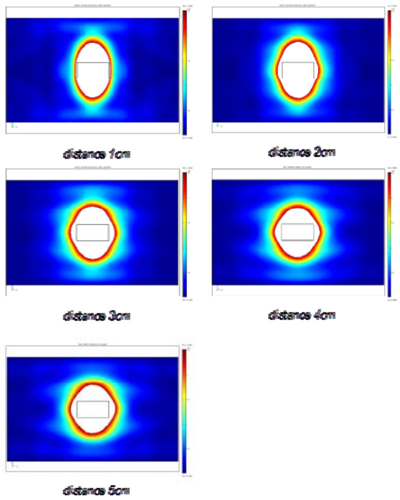

Figure 4.- Sequence heating profile of a wave guide as a function of distance

In order to validate the new microwave curing system, an industrial part was manufactured at pilot plan level. It consists of a 3D panel, which is a section of the hulk of a ship (figure 5).

Figure 5.- Demonstrator MW cured at pilot plant level

4. Conclusions

A multi-functional polyester resin was developed that was suitable for resin infusion and microwave curing. It had a low viscosity for optimal filling of the mould, without curing during the filling process. After filling was completed a microwave system was used to initiate the curing of the resin. The curing was an exothermic reaction, so that the microwave was only necessary to start the process. Specific additives were selected and tested for enhancing the absorption of the material for microwaves. Organic additives with polar properties are most suitable for increasing the absorption without any effect of the material properties. A microwave system was developed which, in connection with a temperature control system, ensured a homogenous heating and therefore curing of the resin. The microwave system was developed with the help of simulations of the microwave field and resultant heating. The degree of polymerization of the resin was increased by using microwaves to nearly 100%. This work was funded by the European Community's Sixth Framework Programme (FP6- NMP3-CT-2005) under grant agreement number 516957.

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