Susceptors improve microwave curing technology for thermosetting resins

The use of microwaves to initiate the curing process of resins is well known. Liquid resins that cure at high temperatures need an increase in temperature to start the polymerization reaction and finally become a solid material. Several methods can be used to increase the temperature, such as conventional heating, ultraviolet radiation, electron beam or microwave radiation. Microwave (MW) curing has two main advantages: 1) heating is volumetric and homogeneous, and 2) curing time is reduced to seconds (so that VOC emissions are also reduced).

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The applications of microwave curing technology include the fabrication of composite parts where the resin cures at high temperature in sectors like railroad, automotive, aeronautics or construction. Due to the advantages of this technology, the main application is the manufacture of large-sized composite parts such as wind turbine blades.

Aimplas developed and studied microwave curing technology in several projects such as MAC-RTM, Wavecom, Code or the ongoing Coaline project. The Coaline European project (www.coaline.eu) received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no.609149. The project started in September 2013 and is coordinated by Aimplas. Its aim is to drastically improve the pultrusion process as the gelcoat will be injected inside the mould, resulting in an in-line, clean one-stage process. In this project, microwave radiation is used to cure the resin in order to reduce the polymerization time and the die length.

The main microwave absorption mechanism in a polymer is the reorientation of dipoles in the imposed electric field. The reorientation makes the polymer's molecules vibrate, thus heating the material. As in a home microwave oven, the materials with the greatest dipole mobility will exhibit the most efficient coupling [1].

Fig. 1: Aeronautics, an application sector for microwave curing technology

Microwave-absorbing additives (or susceptors)

Microwave processing can be used over a broad range of polymers and products, including thermoplastic and thermosetting resins, rubbers and composites. Many polymers contain groups that form strong dipoles (epoxy, hydroxyl, amino, cyanate, etc.), however not all polymer materials are suitable for microwave processing.

In fact, many polymer systems that are candidates for microwave processing (polyester, vinylester, etc.) are typically not conductive and have low polarity. For this reason, conductive particles and fibres or un-reactive organic additives with high electronegativity should be added to the polymer or resin to improve microwave absorption. This mixture creates a complex combination of physical effects that may be included to aid processing or to modify the mechanical, physical, or optical properties. The presence of these inclusions can strongly influence the way the composite material interacts with the microwave radiation. The effect of heating promoters depends on the size, geometry, concentration and electric resistance of the additive or susceptor. It is also very important to achieve a good and homogeneous dispersion of the susceptor in the polymeric matrix.

Some functional groups with a significant dipolar moment can absorb microwave radiation. This dipolar moment represents an electronic cloud distortion between two atoms with dif-

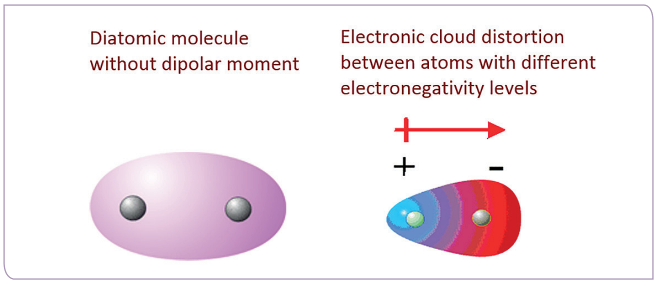

Fig. 2: Molecules without bipolar moment (left) and with bipolar moment (right)

ferent electronegativity levels. If a molecule is composed of only two atoms, a higher electronegativity difference means a higher dipolar moment (figure 2).

Functional groups with strong or medium dipoles include hydroxyls, epoxies, amines, cyanates, imides, chlorine derivatives, etc. Microwave-absorbing additives or susceptors can be divided into three groups: metallic fillers, organic dipolar additives, and inorganic and microwave-transparent additives.

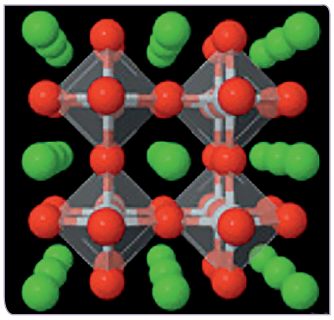

Fig. 3: A common ferroelectric filler: barium titanium

Metallic fillers

Metallic fillers [2] are characterised by an inherent capacity to dissipate electromagnetic energy in the same frequency range as microwaves. The presence of these materials, especially if they are conductive (the majority of metallic fillers), can strongly influence the interaction of the polymer and the microwave radiation. The conductor can also modify the internal electric field pattern as well as other areas affecting the polymer, which causes different heating results to those of the pure polymer. Metallic fillers can be divided into three groups: metals [3], metal oxides and ferroelectric fillers (see figure 3) [4].

Organic bipolar additives

The most studied absorbent functional microwave groups are epoxies, amino, cyanate, isocyanides, hydroxyls, sulphonamides and phthalates, due to the fact that each of them forms strong dipoles. As the main microwave absorption mechanism of a polymer is the reorientation of the dipoles when submitted to an electric field, the presence of these groups in the molecule is necessary.

The materials with the best dipole mobility exhibit high absorption efficiency and the efficiency of the coupling depends on the strength of the dipole, its mobility and mass, as well as its dipole matrix state.

Inorganic and microwave-transparent additives

When additives are inorganic or transparent to microwaves, like for example glass fibres or silicon dust, the electromagnetic make-up will disperse through the charge. Therefore, this effect can modify the heating profile [5].

Assessing the suitability of different MW susceptors

During the COALINE project, different resins and gelcoats were evaluated by adding different susceptors in varying quantities, in order to select the best susceptor and the best conditions. A polyester and a vinylester resin, and a polyester and an epoxy gelcoat were evaluated. Three different susceptors were chosen, named a, b and c, with different percentages. Before microwave curing, the homogeneity of the polymer/susceptor mixtures was characterized to verify the good dispersion of the susceptor into the resin or gelcoat.
The microwave system used is composed of a 2000W magnetron and a cylindrical antenna (figure 4). The frequency of each antenna is 2.45 GHz and the wavelength 12 cm, similar to the conventional microwave devices used at home. The robot can be moved in the three directions using a remote control system.
The evolution of the sample temperature (measured using an infrared sensor over the surface of the resin) versus time at

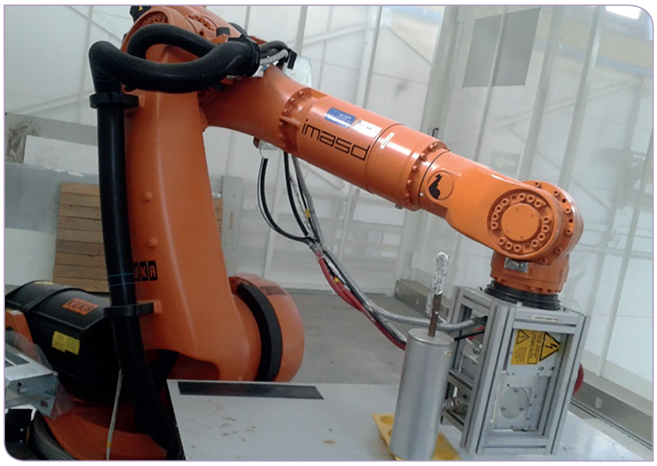

Fig. 4: Open antenna system available at AIMPLAS' facilities

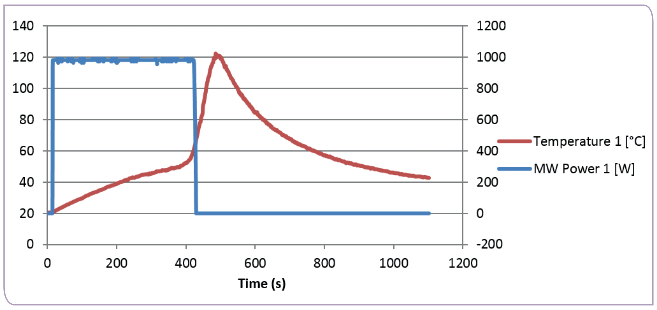

Fig. 5: Temperature and power vs. time for the cure of the polyester resin with susceptor a

Tab.1: Results of MW curing for different resins and gelcoats with susceptors a, b and c

	Time to exothermic peak (min)	Exothermic peak (°C)	Shore D
Polyester resin	12.3	100.5	70
Polyester resin + susceptor a	7.6	122.4	80
Polyester resin + susceptor b	10.6	87.2	80
Polyester resin + susceptor c	**6.0**	125.1	60
Vinyl ester	20.5	112.6	85
Vinyl ester + susceptor a	**11**	70.4	70
Vinyl ester + susceptor b	11.9	95.2	80
Vinyl ester + susceptor c	13.0	72.4	85
Polyester gelcoat	18.9	86.5	80
Polyester gelcoat + susceptor a	**8.7**	94.0	81
Polyester gelcoat + susceptor b	10.2	86.7	70
Polyester gelcoat + susceptor c	13.4	78.0	70
Epoxy gelcoat	13.3	73.0	80
Epoxy gelcoat + susceptor a	6.3	81.5	80
Epoxy gelcoat + susceptor b	4.7	83.8	80
Epoxy gelcoat + susceptor c	**3.8**	83.1	80

constant MW power was recorded for each system (resin and gelcoat with susceptors). An example of the resulting graph can be seen in figure 5.

The graphs were compared in order to choose the most suitable susceptors in terms of interaction with the microwave radiation. 24 hours after the MW curing, Shore D hardness was measured for each sample in order to determine the influence of the susceptors on the mechanical properties of the resin/gelcoat.

Table 1 shows the time necessary for each system to reach the exothermic peak, the temperature of the exothermic peak and the Shore D value of the samples. The addition of susceptors reduces the time needed for the resin to achieve the exothermic peak by 46-71%, which is a very good result.

Fig. 6: MW antenna curing of tensile test pieces with a robot

Tab. 2: Tensile strength results for POLRES 305BV and CRYSTIC VE 676-03 with the best susceptors

Test piece	Maximum resistance (σ)	Deformation (ε)
Polyester resin	9.77 (± 2.34)	0.26 (± 0.11)
Polyester resin + susceptor c	17.1 (± 2.04)	0.26 (± 0.095)
Vinyl ester resin	13.3 (± 3.00)	0.21 (± 0.13)
Vinyl ester + susceptor a	11.4 (± 1.82)	0.19 (± 0.072)

Apart from Shore D, tensile strength was also measured with the best susceptor for each resin (figure 6). The results are shown in table 2. For the polyester resin, it can be seen that susceptor c does not influence the tensile strength properties as the maximum resistance is 7.33 units higher with the susceptor. For the vinylester resin, the results are a bit worse as the maximum resistance with the susceptor is 1.9 units less than for the pure resin, but the standard deviation is 3 units. Then, it can be concluded that the susceptors do not influence the mechanical properties of the resins (tensile strength and shore D hardness).

Conclusions

The addition of susceptors reduces polymerization time during microwave curing of resins and gelcoats. The best susceptors, with the right conditions, make it possible to reduce the polymerization time of resins and gelcoats by 46-71%. The addition of susceptors to improve MW absorption and reduce polymerization time does not influence the mechanical properties of the resins. ■

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