Microwave-assisted Curing of Marine Vinyl ester Resins: Influence on the Mechanical Behaviour

LEONARDO PAGNOTTA
Department of Mechanical Engineering
University of Calabria
Ponte P. Bucci 44C, Arcavacata di Rende (CS)
ITALY

Abstract: - Applications on many thermosets have shown that, with respect to the traditional curing cycles, the microwave-assisted curing always provides a substantial reduction in the curing time. So, it appears a valid alternative process for a faster manufacturing of composite structures in the shipbuilding industry. However, the effects of microwave on the mechanical properties of the materials have not been extensively studied.
In the present paper, a comparison was made between the mechanical behaviour of a vinyl ester resin commonly used for marine applications cured naturally with one cured by microwave. An extensive series of tensile tests indicate that the microwave assisted curing could provide, in a shorter time, strength and stiffness values greater than those obtained by the cure at ambient conditions and that a long exposition to microwave radiation leads to a strength degradation of the resin.

Key-Words: - Vinyl-ester resin, Microwave curing, Curing time effect, Tensile tests, Young's modulus, ultimate strenght

1 Introduction

Fiberglass-reinforced polymer composites are strongly used for the fabrication of hulls, decks and other structures of naval ships and recreational and fishing boats [1-3]. Even if there is a tendency today towards other manufacturing process such as injection and infusion, to improve mechanical behaviour, improve reproducibility, reduce costs and improve working conditions, the open mould process with hand lay-up composite fabrication is still the process more widely used.
The most common used cycle of cure for large naval components is natural curing at ambient conditions. As known, it takes prolonged period of time. Almost always the post-curing process, which is required for completing the crosslinking reactions and then to increase the mechanical properties of the material, is by-passed because of dimensions and costs of the necessary oven. In addition, the conventional thermal curing technology cannot meet the increasing requirements of modern economic development due to its disadvantages of high-energy consumption and long production period. Such reasons well justifies developing of alternative curing techniques, which are expected to be rapid, energy saving, with low operating costs and that allows the better mechanical performances of the material.
It was shown as the typical curing times for thermosetting resins are reduced from hours to minutes by using of microwave rather than conventional curing [4, 5]. This form of energy transfer offers many advantages over conventional heating, such as volumetric, fast, direct, selective, instantaneous and controllable heating with low environmental impact [6, 7]. Microwave heating takes place through dipolar interactions between molecules and an alternating electric field rather than through thermal conduction or convection as in conventional heating. Microwave radiation penetrates materials, and the heat is generated internally.
In order to assess the overall performance of the composite materials, it is essential to understand individually the role of the matrix materials. Resins have the main role of transferring and distributing the applied loads to the fibers, but also to protect them from external damage, prevent fluid access, ensure required electrical properties and hold the fibers together in a structural unit. The matrix properties influence the composite behaviour, its stiffness, strength, failure strain, aging resistance, damage tolerance and temperature behaviour [8]. Mechanical properties of resin systems are greatly

affected by the curing conditions. Studies on epoxy resin system have shown that microwave processing significantly reduces the cure cycle without sacrificing the mechanical properties [9-13]. To the knowledge of the author they are no paper in the international literature giving information about the mechanical behaviour of a vinyl ester resin cured by microwave heating.
The objective of the present paper is to compare the mechanical properties of vinyl ester resins microwave-cured with those of the natural-cured resins.

2 Equipments and experimental procedures

The resin examined in the present study is vinyl ester ATLAC 580 ACT by DSM Composite resins. The initiator used is methyl ethyl ketone peroxide. The added amount is 1.5% by weight.
A mould has been designed for producing the dog-bone resin specimens for tensile testing following standard ISO 527. The mould was made in teflon and consists of a mask reproducing six specimens jointed to a thick plate by a number of plastic screws sufficient to produce a clamping force for preventing the slight seeping of the uncured resin through the gaps between the mask and the lower plate.
Samples of six specimens were prepared and simultaneously cured. Five specimens were addressed to the test machine for determining the tensile properties. The last specimen was used for the determination of polymerization degree obtained by the curing by the differential scanning calorimetry analysis.
Two types of curing process were experienced: natural curing at ambient conditions and microwave curing.
Natural curing was carried out at ambient temperature (around 20 °C) for various time ranging from immediately after the preparation to 1 week.
Microwave curing was carried out using an industrial 6.0 kW microwave oven with an operating frequency of 2450 MHz by Microglass srl Laboratory. Initially, the moulds were exposed to microwave radiation by being placed in the middle of the microwave cavity setting the power at 1500 W. Various samples were cured at different time ranging from 15 min to 4 h.
Tensile tests were carried out according to ISO 527 standard using a universal testing machine (INSTRON 8501) with a MTS load cell of 5 KN. Loading rate was 1mm/minute. For all the tensile tests from three to five specimens were tested per condition. The following tensile tests were determined: tensile strength; tensile modulus; failure strain.
Conventional differential scanning calorimetry (DSC) was used to obtain the enthalpy of cure for the resin. The enthalpy for the cured samples was measured using a Netzsch Fox DSC 200 *F3 Maia®* system. The total enthalpy ΔH_{total} was first measured during cure from the liquid heating at 10 °C/minute up to 240°C samples with weights of about 25 mg sealed in 25 ml aluminium pans. The residual enthalpy ΔH_{peak} was measured heating at 10 °C min^{-1} up to 180 °C solid resin samples extracted from the central part of a cured specimen. 3 samples of each resin were tested for each condition.
The degree of cure, expressed in percent, is defined as the ratio of enthalpies:

$$DoC = \frac{\Delta H_{total} - \Delta H_{peak}}{\Delta H_{total}} 100$$

3 Experimental results

As a first step of the research activity, the behaviour of the resin cured at ambient conditions was studied. Some samples, each of six specimens, were cured at different intervals of time with an exposure time ranging from 6 hours to six days.
It was observed that the value of the degree of cure reaches a 76% within 10 hours. Then, it continues to grow very slowly until its value reaches and stabilizes around a 87% in six days.
It was verified that ultimate strength triples its value passing from six hours (12 MPa) to six days (about 39 MPa) of cure, while the value of stiffness quadruples (increasing from about 0.6 GPa to about 2.5 GPa). Failure strain, on the contrary, decreases of about 15 times.
In a second step of the research, the performances of vinyl ester resin cured by microwave were examined. Samples were exposed to microwave radiation at a power of a 1.5 kW with an exposure time ranging from 15 to 240 minutes.

ISSN: 1790-2769 ISBN: 978-960-474-009-3

It was noted that DoC reaches the 88% after about 75 minutes, successively it grows very slowly with the increase of curing time.
Similarly to the case of natural curing, also in the case of microwave curing, curing time plays an important role on the mechanical properties of the resin.
It can be observed as an increase of the curing times causes a rise of strength and stiffness and a decrease of failure strain, but, also a degradation of the tensile properties can be noted in case of an excessive exposure to microwave. In particular, prolonged exposure to microwave could be detrimental to the tensile strenght.
It was observed that strength and stiffness values of the aged resin are, generally, greater than those measured immediately after the microwave irradiation. Failure strain values, on the contrary, are smaller. Such differences decrease as curing time increase (this behaviour could be justified by taken into account of the increase of the temperature measured inside the microwave oven that accelerates the aging of the resin). As could be expected, a significant increase of DoC in the aged resins was also observed in all the cases in which, immediately after the microwave treatment, DoC values were lower than 87%.

4 Comparisons and discussions

The experimental data versus curing time are illustrated in figure 1. In particular, the graph of figure 1a shows the variation of the degree of cure. It can be clearly seen that the degree of cure increases with the curing time. From the graphs of figures 1b and 1c it can be also observed that the strength and the elastic modulus of vinyl ester grow if DoC is increasing. It can be also observed that, for the same value of DoC, the mechanical properties could have different values depending on the typology of cure adopted. For example, consider the case in which the resin is irradiated by microwaves for approximately 75 minutes. In this case the degree of polarization of the resin reaches about the 87% and it is the same values of resin cured naturally for six days. In these conditions, from the graphs of figure 1, it can be verified that the values of strength and stiffness of the specimens treated by microwave are smaller than those of the specimens cured under natural conditions (in fact, 35 MPa against approximately 40 MPa for the strength and 2 GPa against 2.5 GPa for the stiffness).

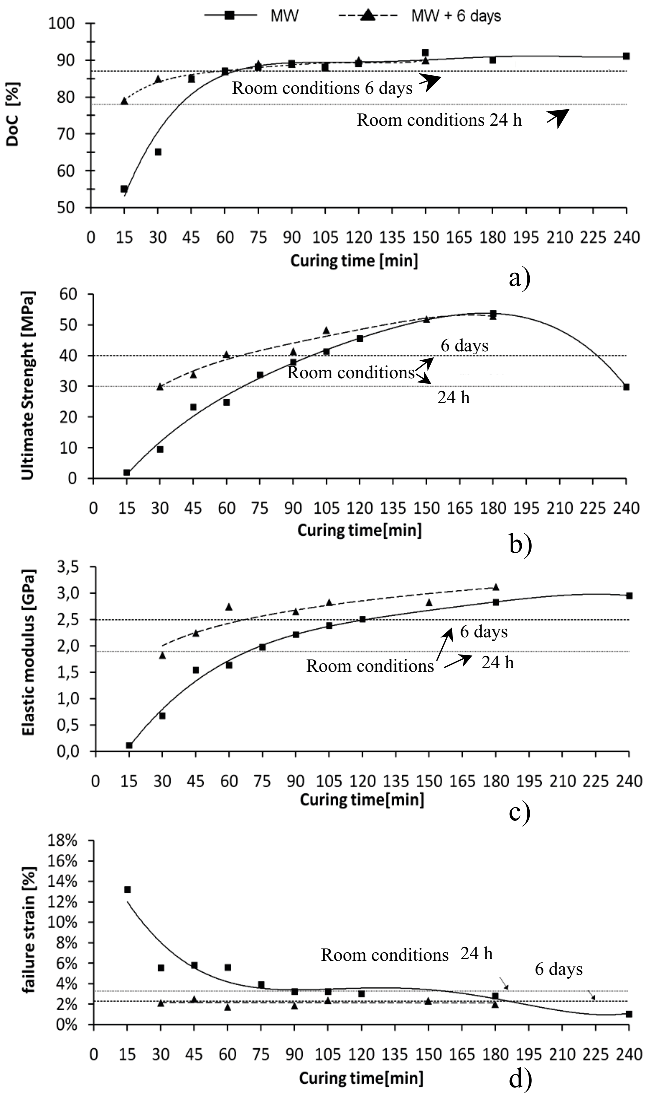

Fig. 1 Vinyl ester behaviour versus curing time: a) degree of cure; b) ultimate strenght; c) Young's modulus; d) failure strain.

From figure 1 it can be also verified that the same value of DoC is reached aging for six day at ambient conditions a resin previously irradiates by microwaves for 45 minutes. In this case both the values of strength and stiffness are smaller than those obtained by a cure under ambient conditions. The discrepancies among such behaviours could be, perhaps, attributed to a different homogeneity of the resin depending on the type and length of curing.
Moreover, from figure 1 it can be noted as the resin cured for 75 minutes by using microwave radiation showed the almost the same mechanical properties of that cured in ambient conditions for 1 day (i.e., about twenty times more quickly). However, the degrees of cure reached were different (85% against 78%). In addition, 105 minutes of microwave irradiation provided to the resin the

same mechanical properties of that obtained with 6 days of natural curing. Curing the resin for 3 hours under microwave radiations (supplied in the microwave oven with a power of 1500 W) provides an ultimate tensile strength and Young's modulus of vinyl ester increasing of 25% and 10%, respectively, with respect to values obtained by a natural curing of 6 days.

5 Conclusions

In the present paper, a comparison was made between the mechanical behaviour of a vinyl ester resin cured naturally with that of a vinyl ester resin cured by microwave. The analysis of the results had confirmed that in both the cases the resin tensile properties depend on the length of curing time. The cure by microwaves provides in a shorter time strength and stiffness values greater than those obtained by the cure at ambient conditions. However, a long exposition to microwave radiation could be detrimental, leading to a strength degradation of the resin.
Vinyl ester resins are rarely used without reinforcement, it is therefore interesting to examine the influence of resin properties on composite behaviour. Some preliminary investigations on the glass fiber/vinyl ester laminates, which results are not reported in the present paper, have shown a mechanical behaviour similar to that of the neat resin. Future work will be focalized on resin reinforced with glass fiber to confirm that expectation. Moreover, to test the real applicability of microwave technology for large component fabrication some studies will be devoted to investigate the scale effects.

Acknowledgements
The author would like to acknowledge and sincerely thank Engineer Quinto Nicoletta from ZEN Marine s.r.l. for supplying necessary specimens and Prof. Fiore Pasquale Nicoletta from University of Calabria for his help on DSC testing.

References

[1] A.P. Mouritz, E. Gellert, P. Burchill, K. Challis, Review of Advanced Composite Structures for Naval Ships and Submarines, *Composite Structures*, Vol. 53, 2001, pp. 21-41.
[2] S. Golpinar, Comparative Analysis of Materials in Recreational Boat Design: Fiber Reinforced Plastic Boat in Serial Production, Thesis for the Degree of Master of Science in Industrial Design, Izmir Institute of Technology, 2005.
[3] A. T. Gunnarsson, Icelandic Boat Builders Switch to Resin Infusion, *Reinforced Plastics*, May, 2004, pp. 34-36.
[4] J. Zhou, C. Shi, B. M., Runzhang Yuan, Z. Fu, Research on the Technology and the Mechanical Properties of the Microwave Processing of Polymer, *Journal of Materials Processing Technology*, Vol. 137, 2003, pp. 156–158.
[5] H. Ku, Curing Vinyl Ester Particle-reinforced Composites Using Microwaves, *Journal of Composite Materials*, Vol. 37, n. 22, 2003, pp. 2027- 2042.
[6] Microwave processing of materials. The National Academic Press, 1994. http://www.nap.edu/openbook/0309050278/html/R1.html.
[7] J.B. Wei, T.Shidaker, M.C. Hawley, Recent Progress in Microwave Processing of Polymers and Composites, TRIP, Elsevier, Vol.4, n. 1, 1996, pp. 18-24.
[8] R.F. Gibson, *Principles of composite material mechanics*. McGraw-Hill, Singapore, 1994.
[9] K.D.V. Prasad Yarlagadda, Shu-Hau Hsu, Experimental Studies on Comparison of Microwave Curing and Thermal Curing of Epoxy Resins Used for Alternative Mould Materials, *Journal of Materials Processing Technology*, 155–156, 2004, pp. 1532–1538.
[10] M. Wallace, D. Attwood, R.J.Day, F. Heatley, Investigation of the Microwave Curing of the PR500 Epoxy Resin System, *Journal of Material Science*, Vol. 41, 2006, pp. 5862-5869.
[11] I. Zainol, R. Day, F. Heatley, Comparison Between the Thermal and Microwave Curing of Bismaleimide Resin, *Journal of Applied Polymer Science*, Vol. 90, 2003, pp. 2764–2774.
[12] D. Zhang, J. V. Crivello, J. O. Stoffer, Polymerizations of Epoxies With Microwave Energy, *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 42, 2004, pp. 4230 – 4246.
[13] S.L. Bai, V. Djafari, M. Andréani, D. François, A Comparative Study of the Mechanical Behaviour of an Epoxy Resin Cured by Microwaves with One Cured Thermally, *European Polymer Journal*, Vol. 31, n. 9, 1995, pp. 875-884.