Proceedings of the International Congress on Ultrasonics, Vienna, April 9-12, 2007, Paper ID 1433, Session R15: NDT: Industrial applications
doi:10.3728/ICUltrasonics.2007.Vienna.1433_lionetto

Air-coupled ultrasonic cure monitoring of composite matrices

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Abstract: The cure monitoring of polymer based materials such as composites, adhesives and plastic coatings is very important in their manufacturing since the degree and rate of curing have a substantial effect on the final product performances. Ultrasound has shown great potential for this application since the changes in the characteristics of propagating waves can be correlated with the real-time mechanical proprieties of a component.

In this work, air-coupled ultrasound in pitch-catch mode has been applied to monitor the curing process of a thermosetting resin both in glass-reinforced laminates and in unreinforced samples. A proper air-coupled ultrasonic set-up has been implemented in order to overcome the signal losses arising during ultrasound propagation through air.

The evolution of the resin mechanical properties during cure is measured by the increase of the ultrasonic velocity, strongly dependent on the cure degree. The technique reliability in monitoring the curing progress has been proved by changing the curing conditions (temperature and promoter content) of the measured samples.

The major advantage of the proposed one-side ultrasonic technique is the absence of physical contact between the transducers and the sample, which is relevant during composite manufacturing, where the direct contact with the probe or the contact with fluid could adversely affect the part quality or the access from both sides is not practicable. No-contact ultrasonic cure monitoring is suitable for both stationary and moving liquid or solid samples in several process conditions such as moulding, filament winding, etc., opening the way to new applications of ultrasound in the composite industry.

Key words: air-coupled ultrasound, composite, cure monitoring, thermosetting matrix

A. Introduction

Air-coupled ultrasound has gained considerable attention over the past two decades thanks to its ability to eliminate the physical contact between the transducer and the material under inspection, which represents the major limit for the use of ultrasonic waves in several industrial processes. However, the difficulties associated with the attenuation of the signal in air and the high acoustic impedance mismatch between air and solid or liquid materials have severe limited the diffusion of this technique.This work presents a novel application of air-coupled ultrasound relative to the cure monitoring of thick samples (7mm) of neat thermosetting resin and glass reinforced resin. It is the first time that this technique is used to follow the strong changes of physical properties occurring during a chemical reaction as the material changes from the liquid to the rubbery and, finally, to the glassy solid state. The proposed technique provides a reliable process control tool for several composite manufacturing technologies (e.g. filament winding, pultrusion and open mould processes).

B. Experimental

B.1. Materials

The studied resin (SIRESTER IS 4240, supplied by SIR Industriale S.p.A.) is an unsaturated polyester resin with a styrene content of 40 wt%. This resin polymerises through a free radical chain mechanism requiring an initiator, to produce free radicals for opening both the resin and styrene unsaturations, and a promoter to accelerate the thermal decomposition of the initiator. The catalytic system used to initiate the curing at room temperature consists of a 50% solution of methyl ethyl ketone peroxide (MEKP) as an initiator, and a 6% solution of cobalt octoate, as a promoter, both supplied by Akzo Nobel.

Glass reinforced laminates (7 mm thickness) have been prepared by hand lay up of 16 plies of glass unidirectional fabrics (Vetrotex) in the 0°/90° configuration.

B.2. Air-coupled ultrasonic set-up

Two non-focussed air-coupled ultrasonic transducers (NCT 75, The Ultran Group) of 500 kHz nominal frequency are placed on the same side of the test material in the so-called “pitch-catch” configuration by a custom-made transducer holder. The NCT 75 have an active diameter of 19 mm and a –6dB bandwidth of 200 kHz.

The transducers are connected to a pulser-receiver device (Epoch 4B, Panametrics), which generates a train of square pulses of 400 V_{pp}. The weak signals from the receiver transducer are fed into a 40 dB preamplifier (Model 5678, Panametrics) before being processed by the pass-band filter of the pulser-receiver device. After the analogue/digital conversion, the signals are displayed on the monitor of a PC, by means of a custom-made software developed with LabView™ (National Instruments).

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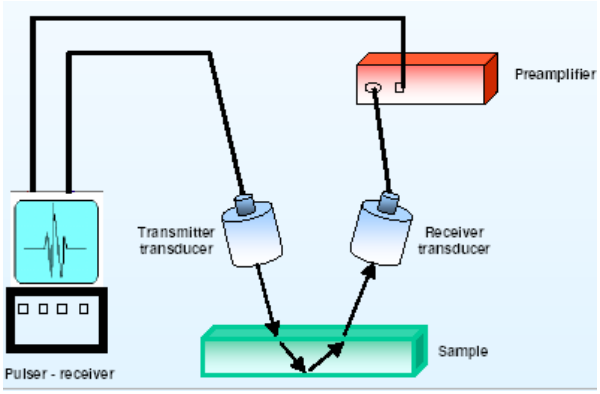

Fig.1. Experimental set-up for the generation and detection of longitudinal waves by air-coupled ultrasound.

As shown in Fig. 1, the non-contact transducers are placed on the same side of the sample, in the so called "pitch-catch" configuration, in which they are not perpendicular to the sample, but held in an angled position by a framework. A suitable angle with respect to the tested material has been chosen in order to achieve the maximum direct transmission. The air gap between specimen and transducers has been between 10 and 20 mm. The geometrical configuration of the air-coupled ultrasonic set-up has been optimised in terms of transducer angles and distances from the sample in order to propagate and detect bulk compression waves through the sample. A detailed description of the geometrical set-up is reported in [1].

The specimen is thus tested by two transducers placed on a single side, making this method very useful for many composite manufacturing technologies, where the access from both sides of the material is not allowed.

C. Results

The novelty of the work here presented consists in the application of the air-coupled ultrasonic technique to the cure monitoring of thermosetting resins. Unlike the conventional ultrasonic evaluation of defects or thickness, the material under inspection undergoes a chemical reaction leading to a significant development of the elastic, and hence acoustic, properties.

The aim of the proposed technique is to single out the two critical stages (gelation and vitrification), occurring during thermosetting polymerisation, whose detection is of fundamental importance during composite manufacturing.

The curing process is characterized by a viscosity increase of the reactive mixture due to the molecular weight growth until *gelation*, when the resin undergoes a transition from a viscous liquid to an elastic gel and the viscosity suddenly approaches infinity. Once the resin has gelled, it cannot be further processed and operations as filament winding, lay up or void removal are no longer possible. The second critical stage during the cure of a thermosetting resin, is the *vitrification*, associated with a continuous increase of the glass transition temperature, which causes the polymerisation end as the glass transition approaches the cure temperature. When the resin vitrifies, it is possible to extract the composite from the mould or mandrel without damaging the component.

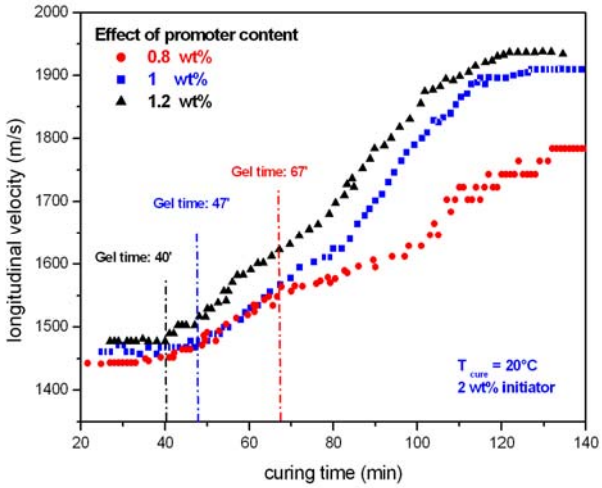

Fig.2. Effect of the promoter content on the temporal evolution of the longitudinal velocity at 20°C for the neat polyester resin.

In Fig.2 the evolution of the longitudinal wave velocity with the curing time is reported for three different catalytic conditions, where only the promoter content slightly changes in order to accelerate the reaction at room temperature (20°C). All the velocity curves are characterized by three zones that can be associated with three different stages of the reaction, as already demonstrated by the same authors by contact ultrasonic results on polyester resins [2]-[3] and epoxy resins [4] although these two kinds of matrices have a different reaction mechanism.

In the first zone, the longitudinal velocity is constant because a high number of reactive groups are present, but the reactive mixture is still liquid and has not yet developed mechanical properties. The onset of the velocity increase can be used as an ultrasonic measurement of gel time [5], in good agreement with the rheological results obtained with a parallel plate rheometer, which are evidenced by the vertical line (dash-dot line) in Fig.2. After the gel point, when the microgel domains are large enough to produce a consistent development of elastic properties, the longitudinal velocity increases rapidly.

In the last region of Fig.2, as a result of the loss in chain mobility due to the increased molecular weight and crosslinking density, the reaction kinetics slows down becoming completely diffusion controlled. The double bond conversion rate is rather low but the mechanical properties continue to develop and can be still followed by means of ultrasound. The longitudinal velocity rises at a lower rate than in the second region and then reaches a plateau value at the end of the reaction process. Since the longitudinal wave velocity is strongly dependent on the material elastic properties, the onset of the final increase can be used as a measure of the vitrification onset, like the onset of the final increase of the shear modulus G' in a dynamic mechanical experiment.

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The overall velocity increment is very high (about 500-700 m/s depending on the curing conditions), indicating that the transition from a viscous liquid to a rubbery material and then to a glassy polymer network is accomplished by a strong acoustic property modification. Due to the good agreement between the longitudinal velocity curves obtained by air-coupled and contact ultrasound, all the already assessed [2]-[5] correlations between ultrasonic velocity and degree of reaction and resin structural changes are valid. This is a further evidence of the sensitivity of the air-coupled technique to detect the physical and structural changes occurring in the curing system at gelation and vitrification.

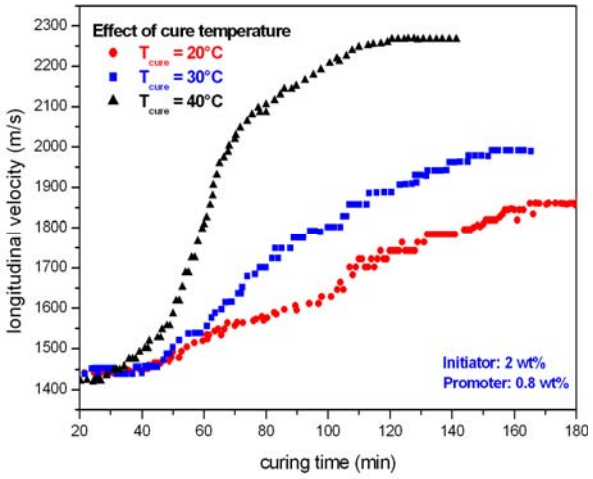

Fig.3. Effect of the cure temperature on the temporal evolution of the longitudinal velocity for the neat polyester resin.

The effect of the cure temperature on the kinetics is shown in Figure 3. As expected, gelation and vitrification times become longer at lower cure temperature and the slopes of velocity curves increases with curing temperature in accordance with the cure kinetics. The ultrasonic results are in agreement with other published data for unsaturated polyester resins obtained by DSC, steady and oscillatory rheology and contact ultrasound [2]-[5].

The technique shows a good sensitivity in detecting the different cure kinetics associated to different promoter contents or cure temperatures.

The good results on neat resin have been confirmed also by those obtained on composite laminates made of unsaturated polyester resins and fiber-glass fabrics. For the composite samples, the presence of reinforcement leads to a reduction of the signal-to-noise ratio because of the scattering of the ultrasonic wave. However, the developed equipment has demonstrated its sensitivity to changes in mechanical properties of composites associated with the cure state of the polymeric matrix.

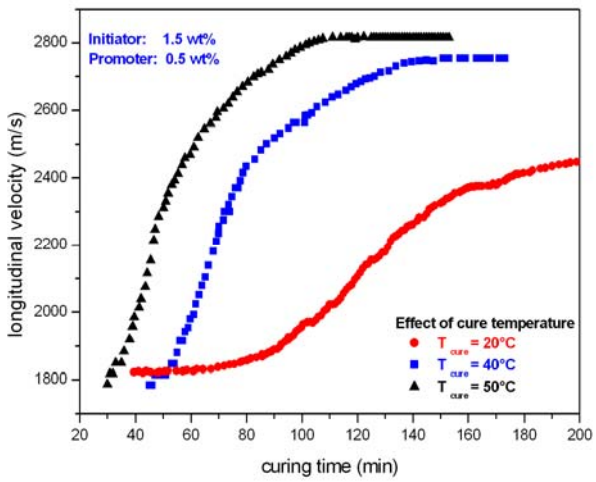

Fig.4. Effect of the cure temperature on the temporal evolution of the longitudinal velocity for the laminate composite (glass reinforced polyester resin).

In Fig.4 is reported the effect of the cure temperature on the temporal evolution of the longitudinal velocity of cross-ply samples cured at different temperatures. Compared to Fig.2 and Fig.3, the values of velocity are higher due to the stiffening provided by fiber-glass. The velocity profile versus cure time is very similar to that observed for neat resin, i.e. it is characterized by a sigmoid behaviour, in which the onset of increase and level off can be associated to gelation and vitrification, respectively.

It should be noted that the curing time reported in the velocity plots has been calculated starting from the mixing of the resin with the initiator and promoter. Therefore, the time lag between the resin mixing and the acquisition of the first ultrasonic data is higher for the composite samples than for neat resin samples, due to the fiber-glass impregnation, the composite lay-up and the measurement setting.

Moreover, for the composite specimens a different catalysis (1.5 and 0.5 wt%) has been used in order to slow down the reaction kinetics, thus increasing the gel time and making possible the composite hand lay up.

D. Conclusion

A custom made air-coupled ultrasonic device has been applied to the cure monitoring of thick samples (7 mm) of unsaturated polyester resin and composite laminates. The progress of polymerization has been monitored through the variation of the time of flight of the propagating longitudinal waves.

The measurements have been carried out at different temperatures and promoter concentrations proving the reliability of this technique in detecting the different polymerization kinetics associated to slight changes of the cure conditions.

The position of the air-coupled transducers on the same side of the sample makes this technique suitable for on-line cure monitoring during several composite manufacturing technologies, where the access from both sides of the material is not allowed.

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E. Aknowledgements

Work funded by the Italian Minister for University and Research (MIUR) under the project L. 297/8341. The authors would like to kindly acknowledge Mr Giovanni Montagna and Francesco Montagna for the software development.

F. Literature

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