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Air-Coupled Ultrasonic Cure Monitoring of Unsaturated Polyester Resins

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Summary: Air-coupled ultrasound in one-side transmission mode has been applied to monitor the curing process of an unsaturated polyester resin, commonly used as a matrix in glass reinforced composites. The evolution of the resin mechanical properties during cure has been measured from the variation of longitudinal velocity. The technique has demonstrated to be a very powerful tool for detecting the structural changes occurring at gelation and vitrification. The no-contact ultrasonic results have been compared with those obtained using conventional contact ultrasonic measurements, characterized by direct coupling between the transducer and the resin, and with the rheological measurements. The good agreement among the results of the different techniques demonstrates the reliability of air-coupled ultrasound in monitoring the changes of viscoelastic properties occurring during the cure of thermosetting polymers. A further 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 probe contact could adversely affect the part quality or 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.

Keywords: air-coupled ultrasound; cure monitoring; gelation; unsaturated polyester; vitrification

Introduction

Unsaturated polyester (UPE) resins play an important role in the composite industry because of their versatility in properties, flexibility in processing and low cost.[1–3] By changing the nature of the unsaturated polyester chain, the styrene/polyester ratio, the catalytic system and curing conditions, UPE matrices are easily tailored to many different specific applications.

The curing of UPE resins is a free-radical copolymerisation between the unsaturated groups of the polyester oligomer and of the reactive solvent (styrene). The unsaturations in the polyester backbone provide sites for free radical addition reaction while styrene is a cross-linking agent for the adjacent polyester molecules. The cure kinetics of polyester resins is normally very complex. The polymerisation is activated by the thermal or photo-induced decomposition of the initiator in free radicals that initially react with the inhibitor present in the resin. The initiator decomposition is accelerated by the presence of promoters, often organic cobalt salts or tertiary amines, which make possible curing processes at room temperature. After the inhibitor is consumed, the free radicals react with polyester and styrene molecules breaking the double bonds.[4]

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Cure monitoring is of great importance for process control and optimisation in composite manufacturing. Ultrasonic wave propagation is a promising non-destructive technique for on-line cure monitoring capable to identify two critical stages during the cross-linking process: gelation and vetrification. The former represents the formation of an elastic gel, while the latter corresponds to the conversion of the gel to a rigid glass. Since these irreversible changes occur at different rates and clearly affect the evolution of the resin mechanical properties, they can be easily detected by ultrasuond.[5–7] Like the rheological methods, the ultrasonic technique follows the cure by monitoring changes in the physical properties of the system, which affect parameters such as longitudinal and shear wave velocities and reflection coefficients. From these parameters, the sample moduli can be calculated.

Despite the potential advantages, the diffusion of ultrasonic cure monitoring in industrial applications is hampered by the necessity of resin-transducer contact in order to propagate acoustic waves into the curing composite without significant losses. At the interface between two materials, only a portion of the sound is transmitted depending on how close are the acoustic impedances of the two materials. Similarly, at the air-solid interface, only a very small fraction of the sound energy is transmitted since air has a very low acoustic impedance. For this reason, the ultrasonic inspection is usually carried out by means of a fluid coupling agent between the ultrasonic transducer and the material under investigation.

The possibility to eliminate the physical contact between the ultrasonic transducer and the resin may extend the application of the ultrasonic wave propagation to several technologies of composite material manufacturing, such as filament winding, pultrusion and open mould processes.

In the last decade, air-coupled ultrasound has been made possible thanks to the development of a new kind of ultrasonic transducers that, minimizing the impedance mismatch between air and transducer, provide a good acoustic transmission also through air.[8] Nevertheless, the potential applications of air-coupled ultrasound have not yet completely explored and there is still a lack of knowledge about this recently developed technique.

In a previous paper,[9] we have presented a custom made ultrasonic set-up for air-coupled ultrasonic monitoring of thermosetting curing. In this work, the developed technique has been applied to study the effect of promoter content and cure temperature on the cure kinetics of an UPE resin. The no-contact ultrasonic results have been compared with those obtained using conventional contact ultrasonic measurements characterized by direct coupling between the transducer and the resin, and with the rheological measurements.

Experimental

Material

The studied resin was a commercial isophthalic unsaturated polyester resin (UPE) with a styrene content of 38% by weight, supplied by SIR Industriale S.p.A. under the commercial name of SIRESTER IS 4240. The number-average molecular weight of the resin was 1338 gmol^{-1} and the average number of vinylene bonds per polyester prepolymer was 4.8. The catalytic system adopted for the cure was based on a 50% solution of methyl ethyl ketone peroxide (MEKP, Akzo) as an initiator and a 6% solution of cobalt octoate (Akzo) as a promoter.

The UPE samples were cured changing the temperature reaction, between 25 and 50 °C, and the promoter content in the reactive mixture. In particular, 2 parts per hundred resin (phr) of MEKP were used for all the samples, while the promoter content was 0.6, 0.8 and 1 phr.

Heat Transfer Conditions

The sample is a slab (100 × 60 mm) with a 7 mm thickness, characterized by 1D heat transfer process. Although the cure of a polyester resin is always coupled with a rapid development of heat, with a good approximation the temperature profile inside the sample can be considered uniform, as results from the calculation of dimensionless diffusive Deborah and Biot numbers.

The isothermal behaviour can be obtained when the dimensionless diffusive Deborah number $De = t_{0.5}{}^{*}k / [\rho C_p (h/2)^2]$ is at least one order of magnitude higher than 1, as reported by Kenny et al.[2] Assuming a resin thickness $h = 7$ mm, a reaction half time of $t_{0.5} = 1920$ s at 50 °C (the most critical temperature), a thermal conductivity of $k = 0.\ 25$ W/mK, a density of $\rho = 1100$ kg/m^3, and a specific heat of 1.3 kJ/kgK, a value of $De = 27 \gg 1$ is obtained. This indicate that the characteristic time for heat generation is much higher than that for heat diffusion and the degree of cure in the sample can be considered uniform.

The Biot number ($Bi = h_c{}^{*}L/k$) represents the relative importance of convective heat transfer at the surface compared to heat conduction within the body.[10] The heat transfer coefficient h_c has been calculated from Nusselt number $Nu = 0.54^{*}(Pr^{*}Gr)^{0.25}$, where Pr is the Prandtl number and Gr the Grashof number, as reported by Kreith[11] in the case of a horizontal slab. Assuming a thermal conductivity of $k = 0.25$ W/mK, and the characteristic length L as the arithmetic media of the sample dimensions (80 mm), a Biot value of 0.18 has been found for the most critical curing condition at 50 °C in the oven. This means that the temperature profile is approximately uniform inside the sample but the heat of reaction can determine an increase of temperature inside the sample leading to non isothermal curing conditions. These results have been also confirmed placing thermocouples in several zones of the resin samples in the same conditions used for ultrasonic measurements.

Air-coupled Ultrasonic Set-Up

Air-coupled ultrasonic measurements were carried out in a custom made ultrasonic set-up (sketched in Figure 1), specifically developed for cure monitoring of thermosetting resins, which has been described elsewhere.[9] Two non-focused air-coupled ultrasonic transducers (NCT 75, The Ultran Group, USA) of 500 KHz nominal frequency, are connected to a pulser-receiver

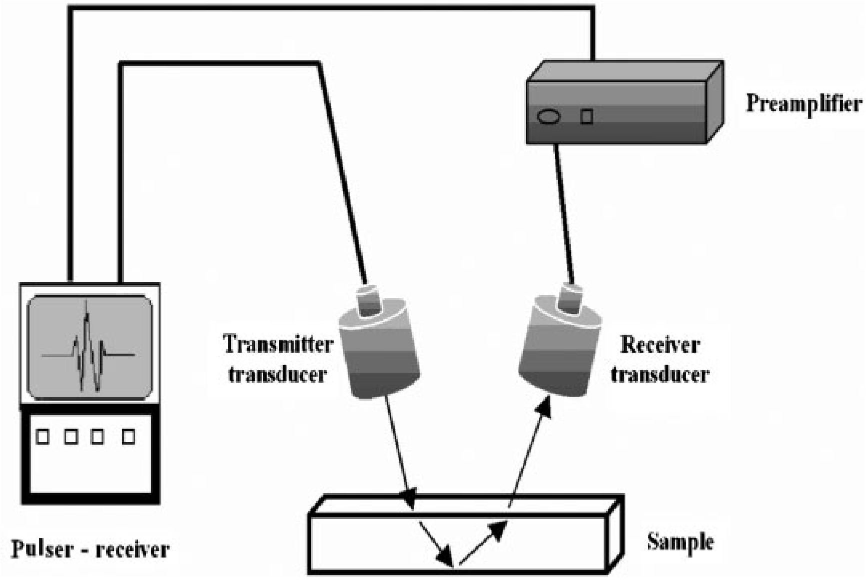

Figure 1.
Sketch of the set-up for cure monitoring by air-coupled ultrasound in one-side transmission mode.

device (Model 9100, Panametrics, USA) and act one as a transmitter (T) and the other as receiver (R). Since the transducers are placed on the same side of the sample, in the so called one-side transmission configuration, the property changes of the bulk of the samples can be measured even if the access from both sides is not allowed, as it happens in most industrial processes during non destructive inspection.

The pulser-receiver device generates a train of square pulses of 400 V_{pp} with a frequency matching that of the transmitter transducer. The weak signals from the receiver transducer are fed into a 40 dB preamplifier (Model 5678, Panametrics, USA) before being processed by the pass-band filter of the pulser-receiver device. This latter provides an analogue/digital conversion of the signal, which can be displayed on the monitor of a PC, by means of a custom made software developed with LabView 6i (National Instruments, USA).

By using a data analysis software, the sample time of flight has been calculated starting from the measured total time of flight, the air velocity and the distance between each transducer and the sample. With the obtained time of flight in the sample, the software can calculate the ultrasonic velocity in the sample, when the path number, the sample thickness, the ultrasound velocity in air and the incident angle of transducer are given as inputs.

For the curing monitoring at high temperature the sample and the transducers have been placed in a oven.

Contact Ultrasonic and Rheological Measurements

Contact ultrasonic measurements were carried out in the through transmission method with longitudinal waves at the frequency of 2 MHz by means of a proprietary ultrasonic apparatus developed modifying a parallel plate rheometer, as described in a previous paper.[7]

Steady and oscillatory rheological measurements have been carried out using a controlled strain rheometer (ARES by Rheometric Scientific) equipped with parallel plate geometry (25 mm diameter). For the steady tests a fixed shear rate of 0.5 s^{-1} has been used, while for the dynamic measurements shear oscillations at 1 Hz and 0.1% amplitude have been used.

Results

In Figure 2 the echoes recorded in air-coupled one-side transmission mode at different times during UPE cure at room temperature are shown. The x axis reports the time of flight, which is the time needed from the ultrasonic wave to travel across the air gap between the sample and the transducers and across the sample. The echo detected in on-side transmission mode, compared to the typical echo signals observed in contact transmission measurements, is broader because it consists of several components generated by different reflection paths through the sample. As widely reported in previous papers,[9,12] these paths depend on the geometrical parameters used for the experiments, i.e. transducer angles and distances, sample thickness, transducer active area.

As observed in Figure 2, during the cure, the ultrasonic echo undergoes significant changes in shape, intensity and position on the time of flight scale. The change in the shape is caused by the disappearing of some echo components relative to the multiple reflection paths inside the sample.[12] Moreover, the decrease in signal intensity is due both to geometrical and physical attenuation effects. The first ones are related to the variation of ultrasonic path in the curing sample, while the second ones are due to the high absorption losses experimented by the ultrasonic waves when interact with the curing system, as observed in contact ultrasonic cure monitoring.[7,13]

From Figure 2 it is evident that the cure progress causes a left shift of the echoes on the time of flight scale. Since the structural changes occurring during cure determine strong variations in the resin elastic properties, the ultrasonic velocity in the gelling and glassy sample increases leading to a

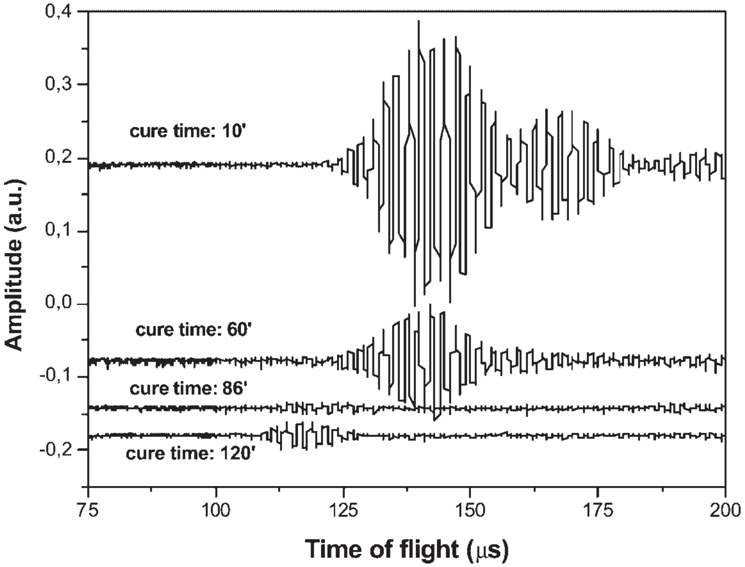

Figure 2.
Echoes detected at different curing stages at 30 °C of a UPE resin sample by air-coupled one-side transmission at 0.5 MHz.

lower time of flight. A reduction of the time of flight can be observed throughout the curing process, as shown in Figure 3, where it is compared with the corresponding evolution of longitudinal velocity.

The ultrasonic velocity curve of Figure 3 is characterized by three zones that can be associated with three different stages of the reaction. In the first zone (I), the velocity is constant during the induction period and the initial part of the reaction, when a high number of reactive groups are present, but the reactive mixture is still liquid and has not yet developed mechanical properties. After the gel point (II), when the microgel domains are large enough to produce a consistent development of elastic properties, the ultrasound velocity increases rapidly. From the comparison of rheological results, the onset of the velocity increase can be used as an indication of gel time, as already reported for contact ultrasonic measurements in transmission mode.[7,13]

At the onset of vitrification, as a result of the loss in chain mobility due to the increased molecular weight and crosslinking density, in the last region the reaction kinetics slows down becoming completely diffusion controlled (III in Figure 3). 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 ultrasonic velocity is strongly dependent on the material elastic properties, the onset of the final increase in velocity can be used as a measure of the onset of vitrification, like the onset of the final increase of the shear modulus G′ in a dynamic mechanical experiment.[14]

The overall velocity increment is very high (about 600 m/s), indicating that the transition from a viscous liquid state to a glassy solid state is accomplished by a strong acoustic property modification. As found for contact ultrasonic measurements,[6,7,13] the air-coupled technique is particularly sensitive to the physical changes occurring in the system towards the end of the reaction, when the reaction rate is extremely low, but the elastic properties continue to increase.

As reported in Figure 4, the longitudinal velocity of curing UPE resin, obtained at

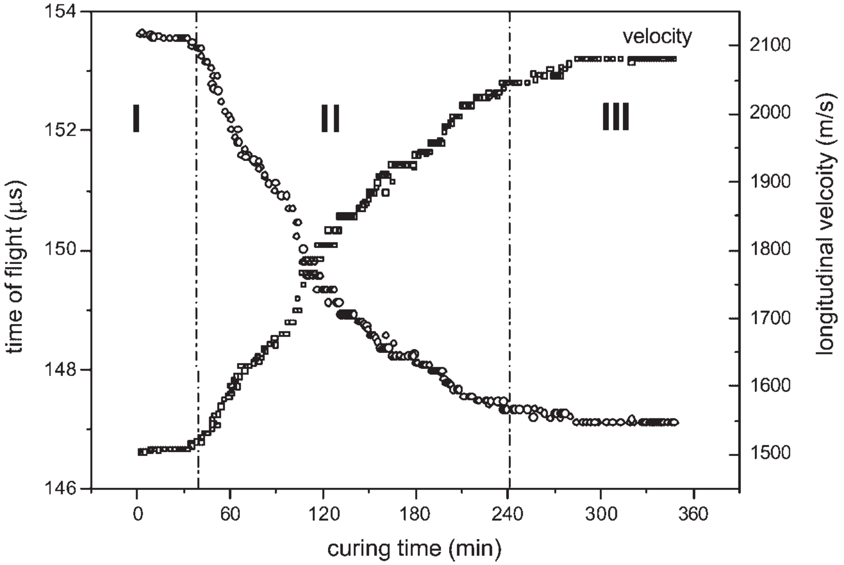

Figure 3.
Evolution of the time of flight and longitudinal velocity as a function of the curing time for UPE cured at 20 °C (0.6 phr promoter, 2 phr MEKP).

room temperature by an air-coupled one-side transmission experiment at 0.5 MHz, is very close to the velocity obtained by a contact ultrasonic measurement at 2 MHz. The ultrasonic contact technique has already proved its validity for cure monitoring of thermosetting matrices, as demonstrated by several papers on epoxy and unsaturated polyester resins.[5–7,13,15–20] For both curves in Figure 4, the onset in the curve increase,

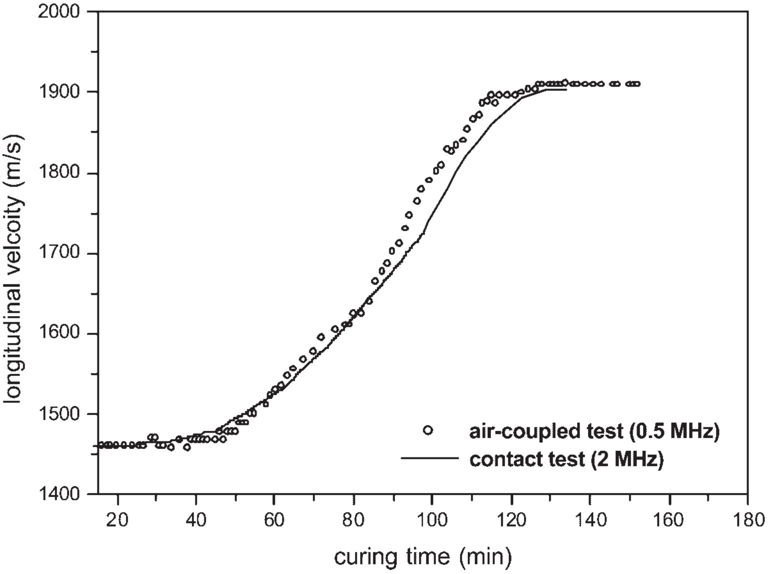

Figure 4.
Comparison between the longitudinal velocity, obtained by air-coupled one-side transmission and contact transmission mode, of an unsaturated polyester resin during curing at room temperature.

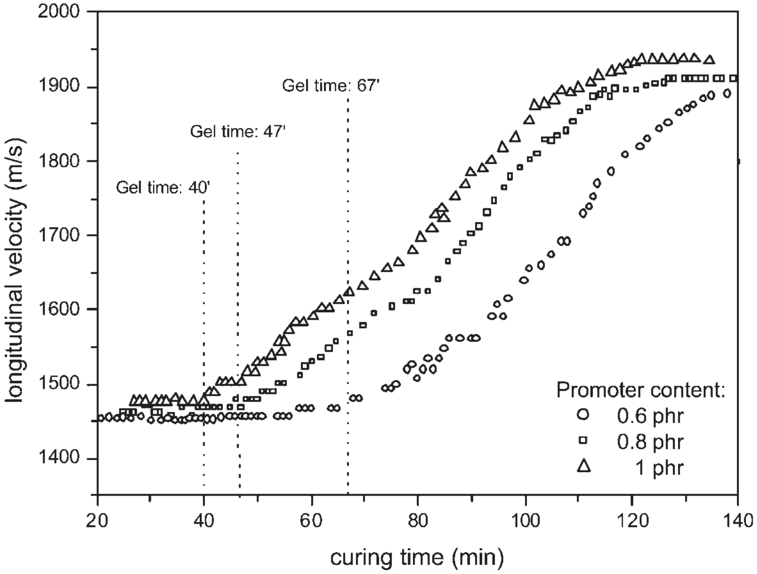

Figure 5.
Effect of the promoter content on the longitudinal velocity during curing at room temperature (2 phr MEKP).

the steep growth, the slow down and the plateau value occur in correspondence of the same cure times.

In this work, the reliability of the developed ultrasonic system in detecting small changes in the cure state has been demonstrated by studying the effect of the cure promoter (cobalt octoate) content (Figure 5) and the cure temperature (Figure 6) on the cure kinetics. As observed in Figure 5, the air-coupled technique is able to single out the different kinetics

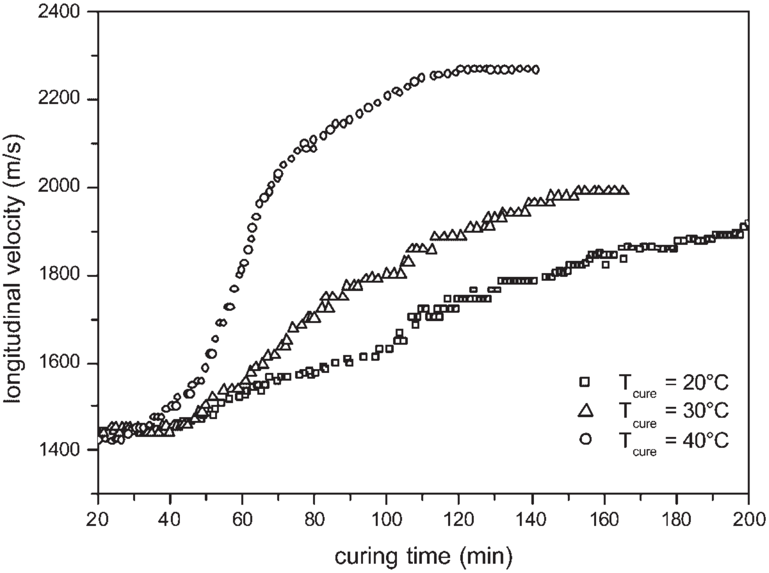

Figure 6.
Effect of the cure temperature on the longitudinal velocity (0.6 phr promoter, 2 phr MEKP).

promoted by small changes in the cobalt octoate content. The promoter activates the cure reaction at low temperatures. A small increase of the promoter concentration leads to shorter gel times and accelerated kinetics. The obtained ultrasonic results indicate that the influence of the initiator/promoter ratio is more pronounced at the start of the reaction than after gelation. This result, obtained with cobalt octoate, well agrees with that found by Salla and Ramis[21] by using tertiary amines as promoter.

The effect of the cure temperature on the kinetics is shown in Figure 6. 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 UPE obtained by DSC, steady and oscillatory rheology[1,22] and contact ultrasound.[12,13]

Increasing cure temperature, the gelation is anticipated but the curve shape changes little. The time at which ultrasonic velocity rapidly starts increasing has been used in this work as a measure of gel time. Being gelation a thermally activated process, the dependence of gel time t_{gel} on cure temperature can be described by an Arrhenius equation[23]:

$$t_{gel} = A \exp(-E_a/RT) \qquad (1)$$

where E_a is the activation energy for the cure, T the absolute cure temperature, A the pre-exponential factor and R the universal gas constant ($R = 8.314$ J/mol*K). The plot of ln t_{gel} (expressed in min) as a function of the reciprocal of absolute temperature (reported in Figure 7) can be used to calculate the activation energy from the slope of the curve.

The ultrasonic results are compared in Figure 7 with those obtained by steady rheology (at a constant shear rate of 0.5 s^{-1}) and dynamic mechanical analysis (at 1 Hz), both performed on a parallel plate rheometer. Activation energies for the cure process of 43.8, 44.7 and 41.2 kJ/mol, respectively obtained from the rheological, dynamic mechanical and ultrasonic results, indicate a good agreement among the different techniques and the literature data (40-60 kJ/mol)[4] for polymerisations

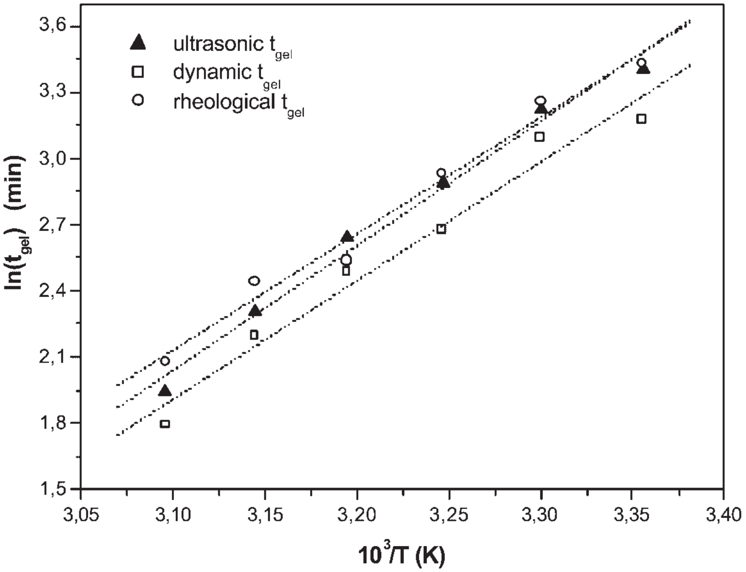

Figure 7.
Activation energy of gelation measured using air-coupled ultrasound, rheology and dynamic mechanical analysis on UPE (0.6 phr promoter, 2 phr MEKP).

promoted by free radicals as in the case of unsaturated polyester resins.

Conclusions

In this work, a recently developed air-coupled ultrasonic technique has been applied to the cure monitoring of an unsaturated polyester resin. The results, obtained without contact between ultrasonic transducers and sample, have shown a full agreement with the well assessed ultrasonic results obtained by contact mode and with those of thermal analysis techniques, routinely used for polymer characterization. This confirms the validity of air-coupled ultrasound for measuring the gelation and vitrification times, which are relevant during composite manufacturing. Once the resin has gelled, in fact, it is no longer processable and operations as filament winding, lay up or void removal are no longer possible. When the resin vitrifies, it is possible to extract the composite from the mould or mandrel without damaging the component.

The implementation of an air-coupled ultrasonic set-up for online cure monitoring could be a powerful tool for quality control. The end of the cure, indeed, could be observed only if the velocity values are within a close range, identifying the composite parts with a partially polymerised matrix. This is a frequent problem in manufacturing of high thickness composites, where, because of a not homogenous heat transfer or errors in resin and catalyst mixing or in formulations, the matrix presents different layers with different degrees of cure and, of course, mechanical properties.

Moreover, the possibility to eliminate the physical contact between the ultrasonic transducers and the resin can extend the application of the ultrasonic wave propagation to several technologies of composite material manufacturing.

Finally, the air-coupled technique used in this work has revealed to be very satisfactory and ready for been implemented in a factory plant for composite manufacturing.

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