ULTRASONIC DYNAMIC MECHANICAL ANALYSIS OF POLYMERS

FRANCESCA LIONETTO*, FRANCESCO MONTAGNA, ALFONSO MAFFEZZOLI

Department of Innovation Engineering, University of Lecce, 73100 Lecce, Italy

* Email: francesca.lionetto@unile.it
Fax: x39.0832.297525

Received: 18.7.2005, Final version: 23.9.2005

ABSTRACT:
The propagation of ultrasonic waves in polymers depends on their viscoelastic behaviour and density, resulting significantly affected by phase transitions occurring with changing temperature and pressure or during chemical reactions. Therefore, the application of low intensity ultrasound, acting as a high frequency dynamic mechanical deformation applied to a polymer, can monitor the changes of viscoelastic properties associated with the glass transition, the crystallization, the physical or chemical gelation, the crosslinking. Thanks to the non-destructive character (due to the very small deformation amplitude), low intensity ultrasound can be successfully used for polymer characterization. Moreover, this technique has a big potential as a sensor for on-line and in-situ monitoring of production processes for polymers or polymer matrix composites. Recently, in the laboratory of Polymeric Materials of Lecce University a custom made ultrasonic set-up for the characterization of polymeric material, even at high temperatures, has been developed. The ultrasonic equipment is coupled with a rotational rheometer. Ultrasonic waves and shear oscillations at low frequency can be applied simultaneously on the sample, getting information on its viscoelastic behaviour over a wide frequency range. The aim of this paper is to present the potential and reliability of the ultrasonic equipment for the ultrasonic dynamic mechanical analysis (UDMA) of both thermosetting and thermoplastic polymers. Three applications of UDMA to different polymeric systems will be reviewed, concerning the cross-linking of a thermosetting resin, the crystallisation from melt of a semicrystalline polymer and the water sorption in a dry hydrogel film. From the ultrasonic velocity and attenuation measurements, the viscoelastic properties of the tested polymers are evaluated in terms of complex longitudinal modulus and compared with the results of conventional dynamic mechanical analysis, carried out at low frequency.

ZUSAMMENFASSUNG:
Die Ausbreitung von Ultraschallwellen in Polymeren hängt von ihrem viskoelastischen Verhalten und der Dichte ab, was in eine signifikante Abhängigkeit von Phasenübergängen, die von Temperatur- und Druckänderungen während chemischer Reaktionen beeinflusst werden, resultiert. Daher kann die Anwendung von Ultraschallwellen mit niedriger Intensität, die als eine hochfrequente dynamisch-mechanische Deformation auf das Polymer wirkt, die mit dem Glasübergang zusammenhängenden Änderungen der viskoelastischen Eigenschaften, die Kristallisation, die physikalische oder chemische Gelbildung und die Vernetzung aufzeichnen. Wegen des nichtdestruktiven Charakters aufgrund der niedrigen Deformationsamplitude können die Ultraschallwellen mit niedriger Intensität als Methode zur Polymercharakterisierung erfolgreich genutzt werden. Darüber hinaus besitzt diese Methode ein grosses Potential als Sensor für die on-line- und in-situ-Beobachtung bei der Verarbeitung von Polymeren und Polymermatrixkompositen. Vor kurzem wurde in dem Laboratorium für polymere Materialien an der Universität Lecce eine Ultraschallapparatur für die Charakterisierung von polymeren Materialien nach Kundenangaben entwickelt, die auch für hohe Temperaturen geeignet ist. Die Ultraschallapparatur ist mit einem Rotationsrheometer gekoppelt. Ultraschallwellen und niedrigfrequente Scheroszillationen können gleichzeitig auf die Probe angewandt werden, um Informationen über das viskoelastische Verhalten über einen breiten Frequenzbereich zu erhalten. Das Ziel dieses Artikels ist, das Potential und die Zuverlässigkeit der Ultraschallwellenausbreitung als eine neue Technik für die dynamisch-mechanische Analyse mit Ultraschall (UDMA) von hitzehärtbaren und thermoplastischen Polymeren vorzustellen. Drei Anwendungen von UDMA auf verschiedene polymere Systeme werden gezeigt, wobei die Vernetzung eines hitzehärtbaren Harzes, die Kristallisation aus der Schmelze eines teilkristallinen Polymers und die Wasseraufnahme eines trocknen Hydrogelfilms betrachtet werden. Aus der Ultraschallgeschwindigkeit und den Dämpfungsmessungen werden die viskoelastischen Eigenschaften (d.h. der komplexe Dehnmodul) der Polymere ausgewertet und mit den Resultaten der konventionellen dynamisch-mechanischen Analyse verglichen, die bei niedrigen Frequenzen durchgeführt wurde.

RÉSUMÉ:
La propagation d'ondes ultrasonores dans les polymères dépend de leur comportement viscoélastique et de leur densité. Elle est significativement affectée par les transitions de phases qui prennent place lorsque la température ou la pression est changée, ou lors de réactions chimiques. Ainsi, l'application d'ultrasons de basse intensité, agissant comme une déformation mécanique dynamique de haute fréquence, peut mesurer les changements de propriétés viscoélastiques associées avec la transition vitreuse, la cristallisation, la gélation chimique

DOI: 10.1515/arh-2005-0016

ou physique, la réticulation. Grâce à son caractère non destructif (due à une amplitude de déformation très petite), la technique d'ultrasons de basse intensité peut être utilisée avec succès pour la caractérisation de polymères. De plus, cette technique a un fort potentiel en tant que capteur pour un contrôle in-situ des procédés de mise en œuvre des polymères ou des composites de matrices polymères. Récemment, dans le laboratoire des matériaux polymériques de l'Université de Lecce, un appareillage expérimental ultrasonique a été développé pour la caractérisation des matériaux polymériques, même à hautes températures. L'équipement ultrasonique est couplé à un rhéomètre rotationel. Les ondes ultrasonores et les oscillations de cisaillement à basses fréquences peuvent être appliquées simultanément à l'échantillon, obtenant ainsi une information sur son comportement viscoélastique sur une large gamme de fréquences. Le but de cet article est de présenter le potentiel et la fiabilité de la propagation d'ondes ultrasonores en tant que nouvelle technique pour l'analyse mécanique dynamique ultrasonore (UDMA) de polymères thermosets et également thermoplastiques. Trois applications de l'UDMA à des systèmes polymériques différents vont être revues, en ce qui concerne la réticulation de résines thermosets, la cristallisation à partir de l'état fondu d'un polymère semi-cristallin, et la sorption de l'eau dans un film sec d'hydrogel. A partir des mesures de la vélocité et de l'atténuation ultrasonores, les propriétés viscoélastiques des polymères testés sont évaluées en termes de module complexe longitudinal et sont comparées avec les résultats de l'analyse mécanique dynamique conventionnelle réalisée à basses fréquences.

Key words: ultrasonic wave propagation, dynamic mechanical analysis, viscoelastic properties, curing, crystallization, water sorption

1 INTRODUCTION

The relatively simple equipment for the generation and detection of ultrasonic waves and the non-destructive character of small amplitudes of vibrations make ultrasonic wave propagation very useful for non-destructive inspection, e.g. for detecting internal flaws, measuring thickness, monitoring the extent of corrosion [1, 2]. Ultrasound is routinely used also in medical imaging and diagnostics and it is finding increasing use in the food industry for both analysis and processing of foods [3 - 5].

Beside the extensive use for non-destructive inspection, ultrasonic wave propagation has also a potential as a characterization technique of materials, especially polymers. In polymers, the propagation of ultrasonic waves is determined by their viscoelastic properties and density and is affected by phase transitions occurring with changing temperature and the other external factors.

Therefore, the application of ultrasound, acting as a high frequency oscillatory excitation applied to the material, is able to obtain information on the polymer viscoelastic behaviour and can be considered as a high frequency extension of dynamic mechanical analysis [6 - 8]. Ultrasonic tests can detect both the macroscopic and microscopic structural changes occurring in polymers by monitoring their viscoelastic behaviour during glass transition, cross-linking, crystallization, physical or chemical gelation. Due to the high frequency and small amplitude of the periodic oscillations applied to the sample, the ultrasonic dynamic mechanical analysis is concerned with the small scale mobility of short chain segments, which generally does not involve the entanglements [9].

However, the application of the ultrasonic technique for polymer investigation has been limited by the insufficient long term stability of transducers at high temperature and the necessity of a fluid coupling medium between the ultrasonic transducer and the sample, since the propagation of acoustic waves in air is poor. A homogenous sample-transducer coupling reduce the transmission losses associated with the propagation of acoustic waves between materials with different acoustic impedance. For these reasons, despite the great potential of low intensity ultrasound as an analysis technique for the characterization of polymer properties, dedicated ultrasonic systems are not yet available on the market.

In the laboratory of Polymeric Materials of Lecce University a custom made ultrasonic set-up, for the characterization of polymeric materials up to high temperatures, has been developed [10]. The system consists of specifically designed narrow-band piezoelectric transducers, propagating longitudinal waves at ultrasonic frequency in the range 1 - 10 MHz, a pulse generator and receiver inserted in a PC and a data analysis software. The ultrasonic equipment is coupled with a rotational rheometer. Ultrasonic waves and shear oscillations at low frequency can be applied simultaneously on the sample, getting information on its viscoelastic behaviour over a wide frequency range.

The aim of this paper is: i) to provide a practical introduction to the use of ultrasonic wave propagation in polymers, ii) to describe the custom made ultrasonic set-up developed in laboratory, iii) to present the results obtained by applying ultrasonic dynamic mechanical analysis for monitoring the changes in viscoelastic properties occurring during the cross-linking of a thermosetting resin, the crystallisation of a semicrystalline polymer and the water sorption process in a dry hydrogel film.

2 BASICS OF ULTRASONIC WAVE PROPAGATION IN POLYMERS

Ultrasonic waves are mechanical vibrations that propagate through a material as a series of very small displacements of atoms and chain segments from their equilibrium positions. Because of the forces within a chain segment and between adjacent chain segments, displacements are continuously induced at neighbouring zones, thus creating stress waves propagating through the material [2]. Several kinds of ultrasonic waves may propagate in polymers, such as longitudinal waves, shear waves, Rayleigh waves (or surface acoustic waves), Lamb waves (or plate waves). The most common methods of ultrasonic examination use either longitudinal or shear waves.

In an acoustic sense, a material is fully characterized by two parameters: the ultrasonic velocity *c* and the ultrasonic attenuation *a*. The first is the velocity of propagation of elastic waves and is calculated on the basis of the measured time of flight, that is the time taken by the sound to travel through the sample. Sound velocity through a material depends on its density and viscoelastic properties. Attenuation is a measure of dissipative energy loss (converted to heat) as the wave travels through the polymer. These energy losses are due to the absorption and scattering of ultrasonic waves. The scattering contribution is considerable when the medium is non-homogeneous and contains particles comparable in size to the ultrasonic wavelength, such as in filled polymers or in semicrystalline polymers. The absorption is related to molecular rearrangements in the polymer structure, such as glass transition, melting, crystallisation, and to chemical reactions such as those occurring during curing. Just as in dielectric tests, energy absorption is related to damping, loss factor and loss tangent [9]. Attenuation is determined by the changes in the amplitude of the acoustic signals.

The acoustic response of a material can provide information on its mechanical properties. During an ultrasonic experiment, the complex longitudinal or shear moduli can be calculated, when longitudinal or shear waves propagate through the sample, respectively. Nevertheless, the propagation of shear waves is restricted by the very high damping properties of polymers, often leading to a complete attenuation of the wave through the sample [6]. On the other hand, the propagation of longitudinal elastic waves is easily observed in polymers as well as in reactive liquid mixtures of monomers.

Depending on the nature of the ultrasonic wave, from measurements of velocity *c* and attenuation *a* the components of the complex shear or longitudinal modulus (here indicated easily with *M'* and *M''*) can be calculated according to the following equations [7, 11]:

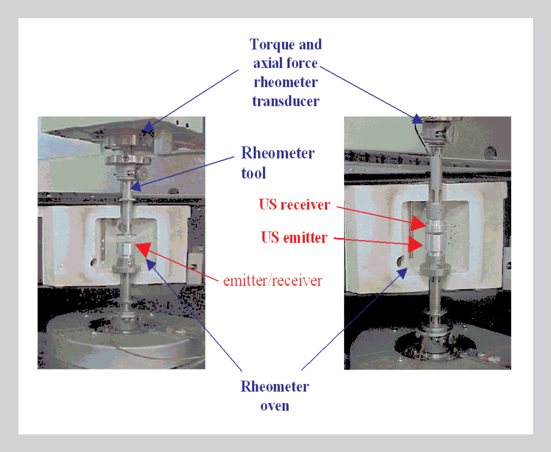
$$M' = \frac{\rho c^2 \left[1 - \left(\frac{a\lambda}{2\pi}\right)^2\right]}{\left[1 + \left(\frac{a\lambda}{2\pi}\right)^2\right]^2} \quad \text{and} \quad M'' = \frac{\rho c^2 \left(\frac{a\lambda}{2\pi}\right)}{\left[1 + \left(\frac{a\lambda}{2\pi}\right)^2\right]^2} \tag{1}$$

where ρ is the material density and λ is the wavelength of propagation, given by the ratio between velocity and frequency f($\lambda = c/f$). When $a\lambda/2\rho$, << 1, i.e. when the attenuation per wavelength is small, as in most practical applications, the following simplified formulas can be used:

$$M' = \rho c^2 \quad \text{and} \quad M'' = \frac{\rho c^3 a}{\omega} \tag{2}$$

where ω is the angular frequency ($\omega = 2\pi f$).

In particular, when bulk longitudinal waves propagate in a sample with the dimension normal to the acoustic wave large compared to the wavelength, the measurement of ultrasonic velocity and attenuation may be used for the calculation of the storage, *L'*, and loss, *L''*, longitudinal moduli, which are related to the bulk (*K'* and *K''*) and shear (*G'* and *G''*) moduli according to the



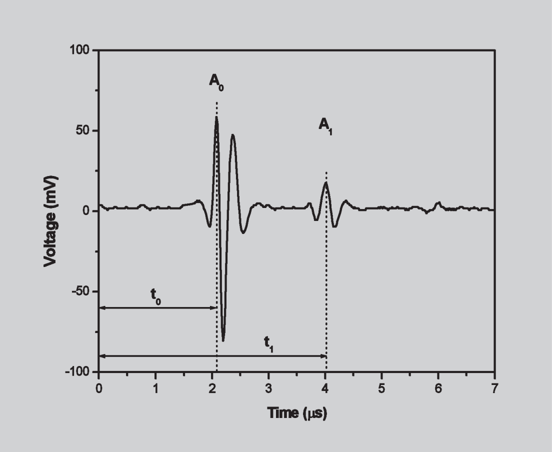


Figure 1 (left): Ultrasonic probes fitted into the fixtures of a parallel plate rheometer (Rheometric Scientific): pulse-echo (left) and transmission (right) configuration.

Figure 2: Reflected echoes from the interface between transducer delay line and polymeric sample (echo A_O) and from the interface between the sample and the rheometer plate (echo A_1).

equations valid in conditions of plane strain (i.e. the strain in one direction is zero) [11]:

$$L' = K' + \frac{4}{3}G' \tag{3}$$

$$L'' = K'' + \frac{4}{3}G'' \tag{4}$$

L' corresponds to the stiffness of a system that is deformed changing its dimensions in one direction while in the other two directions the dimensions are constrained to be constant, as it occurs in samples where two dimensions are much larger than the third [11].

3 ULTRASONIC EXPERIMENTAL SET-UP

The ultrasonic apparatus, developed in the laboratory of Polymeric Materials of Lecce University, consists of two specifically developed piezoelectric transducers, propagating longitudinal waves at ultrasonic frequency in the range 1 - 10 MHz. The transducers are fitted into the tools of a parallel plate rheometer (ARES, Scientific Rheometric) and connected with a pulse generator and receiver integrated in a personal computer. The pulser-receiver generates a pulse train, amplifies the signal transmitted through the sample and provides an analogue/digital conversion of the signal, which is sampled every 10 s and displayed on the monitor of a computer using a LabView based analysis software.

The experimental set-up can be used in a very broad temperature range (from – 50 to 250°C), which covers great part of the investigation range of many polymers. The withstand to high temperatures is assured by the active element of the ultrasonic probes, which is different from the materials commonly used for non destructive inspection. The piezoelectric transducer, indeed, can work up to 250°C without loosing his piezoelectric properties.

The polymer sample, in the form of a disc (30 mm diameter and 2 mm thickness) is sandwiched between two ultrasonic probes fitted into the oven of the rheometer. The contact pressure between probes and sample and the sample thickness are controlled by the vertical movement of the upper transducer, driven by the gap control function of the rheometer, while the temperature is controlled by the forced air environmental controller of the rheometer oven. The insertion of the ultrasonic probes in the rheometer provides a great accuracy in the control of the sample thermal behaviour and thickness. In particular, a great accuracy in the determination of the actual sample thickness assures a great accuracy in the calculation of the actual values of velocity and attenuation during the experiments.

Moreover, the coupling between ultrasonic system and rotational rheometer leads to a deeper analysis of the sample viscoelastic behaviour over a broad frequency range, making possible to perform at the same time a dynamic mechanical experiment at low (1 - 5 Hz) and ultrasonic (2 - 10 MHz) frequencies. The ultrasonic set-up for polymer characterization can work both in pulse-echo and in transmission mode. The ultrasonic probes, fitted into the fixtures of the ARES rheometer, are displayed in Fig. 1, both in pulse-echo and transmission configuration.

In pulse-echo mode, a single transducer propagates and receives longitudinal waves, normally incident on the specimen surface. The typical signal obtained is displayed in Fig. 2. The ultrasonic wave, created by the transducer, undergoes a first reflection at the interface between the transducer delay line and the sample, generating a first echo of amplitude A_O. The remaining part of the wave, instead, continues travelling through the sample until it reaches the interface between the sample and the rheometer plate, where a considerable fraction of it returns back to the transducer. The received oscillations are converted by the transducer into an electrical pulse and displayed as a second echo of amplitude A_1 (Fig. 2).

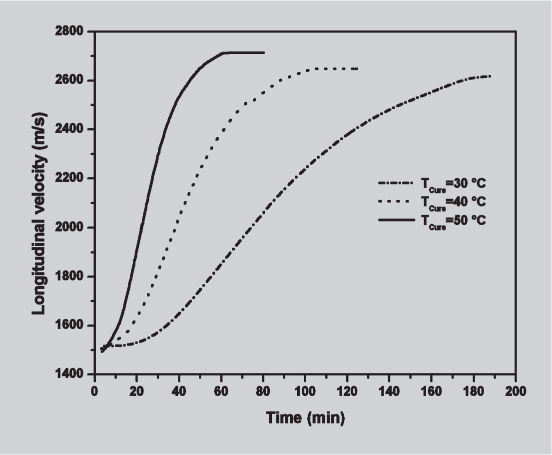


Figure 3 (left): Longitudinal velocity measured at 2 MHz during the isothermal cure of UPE resin at different temperatures.

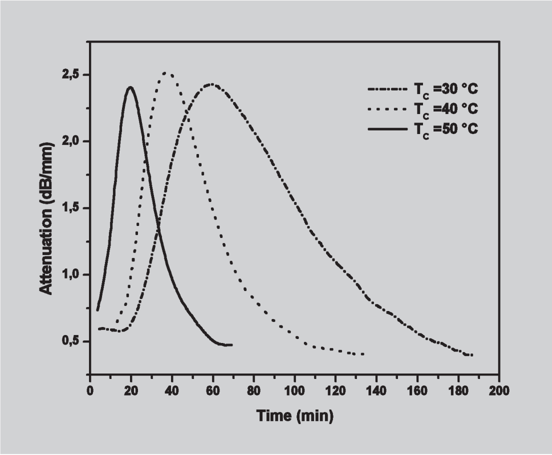


Figure 4: Ultrasonic attenuation measured at 2 MHz during the isothermal cure of UPE resin at different temperatures.

The two echoes are relatively spaced by a time *t*, called “time of flight”, which is the time necessary for the ultrasonic wave to travel across the sample. The wave time of flight relates to the elastic properties of the sample, i.e. to its ability to transmit longitudinal waves. Moreover, the two echoes displayed in Fig. 2 have different amplitudes because the ultrasonic wave, during its travel through the sample, undergoes an attenuation depending on the material damping capacity. The temporal distance between two successive echoes and their amplitude ratio are important parameters for assessing the sample acoustic behaviour through the calculation of the velocity and attenuation of the ultrasonic waves.

In transmission mode, two probes are used, one as a transmitter and the other as a receiver. The ultrasonic waves, generated by the emitter transducer, travel through the sample and reach the second piezoelectric transducer (receiver). The received signal is displayed as an echo. If a good coupling between sample and transducer is assured by means of a fluid coupling agent, the transmission losses associated with the propagation of acoustic waves between materials with different acoustic impedance are very low; in this way, only a small part of the ultrasonic wave is reflected back to the transducer, the major part is transmitted.

The time of flight of the echo signal and the attenuation are determined by comparison of the peak time and peak amplitude of the transmitted wave with those of a reference signal, recorded with the two transducers in contact without sample.

4 EXPERIMENTAL RESULTS

4.1 CURE MONITORING OF THERMOSETTING RESINS

The non-destructive character of ultrasonic waves and the possibility to use these as on-line sensors, make this technique suitable for the monitoring of the curing of thermosetting resins in the processing of composite materials and for predicting their final properties [9, 12 - 19].

The ultrasonic technique can identify the two critical stages of the cross-linking process, respectively called gelation and vitrification. The first stage represents the formation of an elastic gel, while the second one 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 ultrasonic techniques [16 - 17].

The results, reported here, are based on studies of the cure of an unsaturated polyester resin, used as a matrix for glass-reinforced composites. This resin, supplied by SIR Industriale S.p.A. (Italy) under the commercial name of SIRESTER IS 4240, has a styrene content of 38 wt%. The catalytic system adopted for the cure is based on a 50% solution of methyl ethyl ketone peroxide as an initiator and a 6% solution of cobalt octoate as a promoter, used, respectively, at 1.5 and 0.5 parts per hundred parts of resin (phr).

The ultrasonic velocity curve (Fig. 3) shows three zones that can be associated with three different stages of the reaction. In the first part of the curve, the ultrasonic 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, the longitudinal velocity increases rapidly due to the crosslinking and the evolution of the resin mechanical properties. The velocity increase continues until a plateau value is reached, corresponding to the slowdown of the reaction as a result of the vitrification. The overall velocity increment is very high, indicating that the transition from viscous liquid state to glassy solid state is accomplished by large changes in acoustic properties. The slope of longitudinal velocity curves increases with curing temperature in accordance with the cure kinetics.

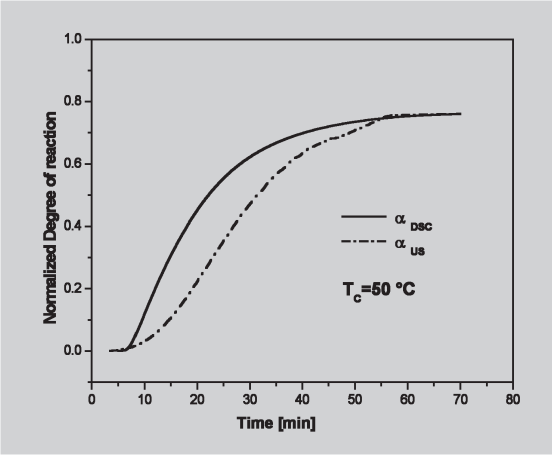


Figure 5: Normalised degree of reaction calculated from DSC and longitudinal modulus (measured at 2 MHz) for an UPE resin during the isothermal cure at 50°C.

The curve of the ultrasonic attenuation versus cure time (Fig. 4) is bell-shaped. The attenuation increases during the first steps of the sol-gel transition, showing a distinct peak that arises from vitrification of the resin, when the glass transition temperature, continuously increasing during the cure, becomes equal to the cure temperature. In correspondence of the glass transition, it is possible to detect a peak in the loss modulus, in the loss factor, in the dielectric loss and also in the acoustic attenuation. Increasing the cure temperature of the samples, the attenuation curves become narrower and the time corresponding to the attenuation peak is anticipated.

In order to analyse the progress in the cure reaction of unsaturated polyester resin, a DSC analysis, both in isothermal and non-isothermal conditions, was carried out. It is postulated that the amount of heat generated through curing can be directly related to the conversion of the reactive groups. In isothermal DSC experiments, the degree of reaction α_{DSC} is calculated as:

$$\alpha_{DSC} = \frac{\Delta H(t)}{\Delta H_{TOT}} = \frac{1}{\Delta H_{TOT}} \int_{o}^{t} \frac{dH}{dt} dt \qquad (5)$$

where $\Delta H(t)$ represents the partial heat of reaction developed during an isothermal DSC experiment and ΔH_{TOT} is the maximum heat of reaction measured in non-isothermal experiments, taken as a reference value. The results of the calorimetric and ultrasonic measurements can be compared on the basis of a normalized degree of reaction obtained from curing experiments at the same temperature. The ultrasonic degree of reaction α_{US}, assessed by ultrasonic measurements, can be calculated according to the following equation:

$$\alpha_{US} = \frac{L' - L_o}{L'_{max} - L'_o} \alpha_{DSC_{max}} \qquad (6)$$

where L'_O and L'_{max} are respectively the minimum and the maximum value of the longitudinal modulus L' and α_{DSCmax} is the ratio between the isothermal heat (ΔH_{ISO}) and the maximum heat of reaction (ΔH_{TOT}), measured by DSC by dynamic ramps at 10°C/min.

The comparison between the normalised degrees of reaction from ultrasonic and calorimetric experiments in isothermal conditions is shown in Fig. 5. At the beginning of the cure, the degree of reaction measured by DSC increases more rapidly than the ultrasonically measured value, since the mechanical properties of the resin before the gel point are scarcely affected by any increase in molecular weight. At gelation, the growing network gives rise to a significant increase of velocity. During the later stages of the cure, significant changes in the longitudinal velocity and modulus L' occur, while the degree of cure is fully developed and remains nearly constant. There is a non-linear correlation, therefore, between longitudinal modulus and degree of cure.

The longitudinal modulus L' shows a strong sensitivity to the last part of the cure, where a significant increase of the crosslinking density occurs. In a crosslinked structure, the cure, involving the reaction of a limited number of reacting groups in a glassy polymer, is diffusion controlled and cannot be observed by DSC but may be studied by means of propagation of ultrasonic waves [9, 16 - 17]. Ultrasonic wave propagation can be used also to monitor isothermal and non-isothermal post-cure cycles during manufacturing of composite materials [20]. In particular, by combining ultrasonic and low frequency DMA results, it is possible to get a better insight of the relaxation phenomena over a wide frequency range.

4.2 NON ISOTHERMAL CRYSTALLIZATION OF SEMICRYSTALLINE POLYMERS

The ultrasonic technique can be also used to monitor the crystallization process of semicrystalline polymers, both in isothermal and non isothermal conditions since this technique is sensitive to detect the changes in acoustic properties associated with the growth and nucleation of crystals. The developed ultrasonic set-up has been successfully used to study the crystallization of a biopolymer (wheat starch) in isothermal conditions [21], but, for sake of brevity, in this paper we report only the ultrasonic monitoring of the crystallization of linear low density polyethylene during cooling from melt.

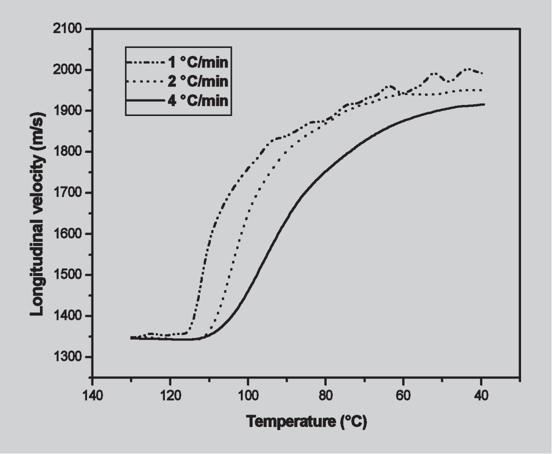


Figure 6 (left): Longitudinal velocity measured at 2 MHz during non-isothermal crystallization of LLDPE at different heating rates.

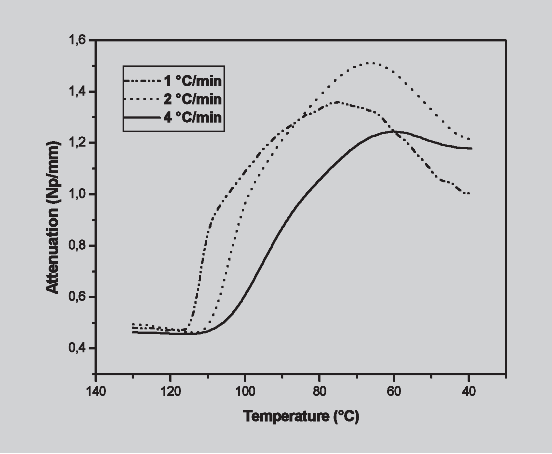


Figure 7: Ultrasonic attenuation measured at 2 MHz during non-isothermal crystallization of LLDPE at different heating rates.

With respect to the previous ultrasonic studies on crystallization carried out by other workers [22 - 25], the novelty of the presented results consists in the possibility to measure L^* and G^* in the same experiment using the same rheometer with a little modified parallel plates. Using the ultrasonic probes (having a cylindrical shape) as parallel plates of a rotational rheometer, it is possible to superimpose low intensity longitudinal waves at 2MHz and shear oscillations at 1 Hz, carrying out simultaneously a dynamic mechanical experiment at ultrasonic and low frequencies.

Samples of linear low density polyethylene (LLDPE), supplied by Polimeri Europa (Italy) under the commercial name of Clearflex RM50, were heated to 150°C between the ultrasonic probes within the rheometer oven and kept for ten minutes at this temperature for complete melting. Then, the polymer was cooled at different rates between 1 and 4°C/min.

The high shrinkage of the LLDPE sample, resulting from the high rate of crystallization, was counterbalanced by the auto-tension function of the rheometer, which assured a constant value of contact pressure between ultrasonic probes and sample varying the distance between the two ultrasonic probes in accordance with the material contraction.

During cooling, the longitudinal velocity (Fig. 6) remains constant for temperatures higher than the crystallization temperature, and then follows a sigmoid behaviour, as reported also by other authors [22 - 25]. In correspondence of the onset of crystallization, an abrupt increase in the velocity can be observed. As confirmed by other experimental techniques, the onset of crystallization strongly depends on the cooling rate and shifts towards lower temperatures with increasing cooling rates [26]. At lower temperatures, a slow growth regime can be distinguished in the longitudinal velocity curve.

The growth of ordered crystalline fractions produces stronger intermolecular interactions, leading to increased mechanical properties and, consequently, to an increase of sound velocity during non isothermal crystallization. The growth of LLDPE elastic properties is reliably monitored by the increase of longitudinal velocity even at low temperatures, when only crystal perfection phenomena occur. Therefore, the ultrasonic wave propagation can be successfully applied to study also the end of the crystallization process.

The attenuation, as reported in Fig. 7, remains constant before the onset of crystallization and then exhibits a very rapid increase followed by a peak and a slow decrease. It should be noted that semicrystalline polymers can be considered to be heterogeneous due to the presence of crystallites, causing sound wave scattering depending on wave frequency and crystallite average size D_O. If the wavelength λ is much higher than D_O ($\lambda >> D_O$), the scattering contribution to attenuation can be neglected and the crystallites are too small to affect the sound waves. In this case, the attenuation results from the absorption associated with the viscoelasticity of the amorphous phase. When $\lambda \approx D_O$ or $\lambda < D_O$, attenuation is primary due to scattering phenomena [6, 27 - 28]. Therefore, the attenuation increase, due to scattering phenomena, occurs when the developing crystallites reach a critical size comparable with the wavelength.

As the temperature decreases further and the crystalline fraction increases accordingly, the attenuation decrease is mostly due to the reducing absorption of the amorphous phase. At the same time, the scattering losses are also very low, due to the formation of a single stiffer crystalline phase, with dimensions much larger than the wavelength. The peak in the attenuation is observed at lower temperatures with increasing cooling rate.

The comparison of L' and G' obtained from a simultaneous low frequency (1 Hz) DMA and high frequency (2 MHz) ultrasonic experiment, carried out during a cooling at 2°C/min, is reported in Fig. 8. In this experiment, the ultrasonic probes work both as transducers, for transmission and

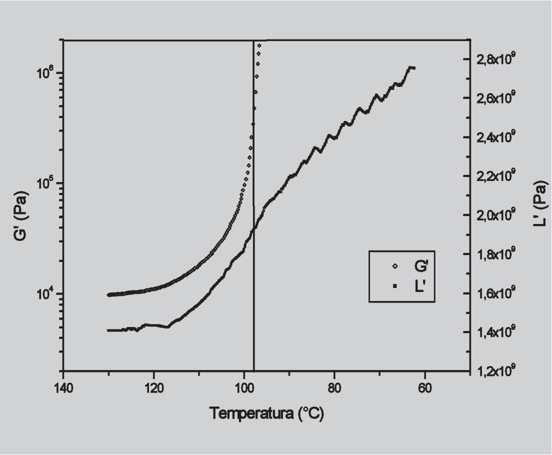


Figure 8 (left): Comparison between the storage longitudinal L' (at 2 MHz) and shear G' (at 1 Hz) moduli obtained during non-isothermal crystallization of LLDPE at 2°C/min.

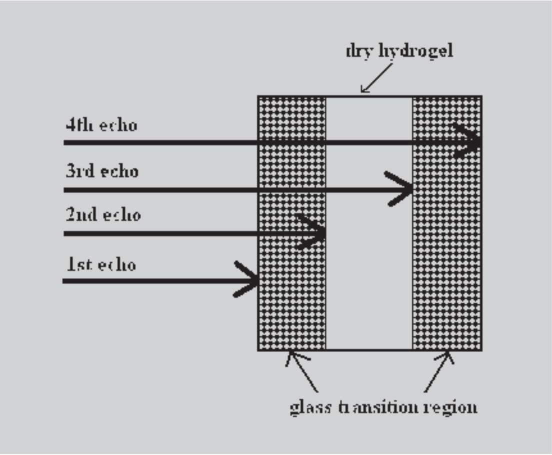


Figure 9: Schema of the water sorption process in dry hydrogels.

detection of ultrasonic waves, and as parallel plates of a conventional rotational dynamic mechanical analyzer, i.e. one of the probes rotate alternatively applying small shear oscillations to the sample. It should be kept in mind that the oscillations applied by the two techniques are different both for frequency and strain direction. In this work, the ultrasonic technique applies longitudinal waves, i.e. a series of compression waves with a 2 MHz frequency, whereas the low frequency DMA applies shear oscillatory deformations at 1 Hz. The intensities of both the deformations are very low and within the limit of linear viscoelasticity of the sample.

A great difference between the magnitude orders of *L'* and *G'*, calculated independently as if there was no coupling, is expected if one accounts that for melt polymers $G' << K'$ and, consequently, $L' \approx K'$. As shown in Fig. 8, low frequency DMA cannot monitor the last part of the crystallization process. At low temperatures, indeed, because of the high sample rigidity caused by the growth of crystallites, the measurement of shear modulus is critical. To avoid transducer over-loading, the DMA experiments cannot be continued at temperatures below 100°C. This limit is overcome by ultrasonic technique, which demonstrates to be able to monitor crystallization process from beginning to the end.

4.3 WATER SORPTION IN DRY HYDROGELS

The third case study, presented in this review paper, concerns the application of ultrasonic waves to monitor the water sorption process in dry hydrogels. This application represents a novel approach to study the kinetics of water sorption in polymers, till now carried out by means of weight, dimensional change or dielectric measurements.

Water sorption in dry hydrogels, being associated with significant changes of density and elastic constants of materials, can be monitored by ultrasonic wave propagation [29 - 31]. Water sorption in a glassy polymer immersed in water can be approximately divided into two main steps: the advancement of a swollen front, from the sample boundaries towards the centre, and the diffusion of the solvent in the swollen matrix. Water acts as a plasticizer, reducing the glass transition temperature of the polymer below the sorption temperature and determining a glass rubber transition in the hydrogel at the sorption front. The propagation of ultrasonic waves through the hydrogel during water sorption is characterized by reflections at the glassy-rubbery fronts as well as absorption in correspondence of the swollen-unswollen fronts undergoing a glass transition.

The ultrasonic results, reviewed here, were obtained by Maffezzoli et al. [29] monitoring by pulse-echo technique the position of the swollen-unswollen fronts and measuring ultrasonic velocity and attenuation in dry Poly-vinyl-alcohol (PVA) hydrogels during water sorption. PVA films (1 - 1.5 mm thickness) were prepared by drying a diluted solution (9% by weight) under vacuum at 50°C for 36 hours. The monitoring of the water sorption process was obtained at 25°C by immersion of the sample and ultrasonic transducer in distilled water.

At the beginning, only two liquid-dry hydrogel interfaces are present. Then, during water sorption, two new interfaces are created causing a growth of attenuation because these portions of material undergo a glass transition (Fig 9). The presence of four interfaces in the sample causes multiple reflections, as also revealed by the detected four echoes, reported in Fig. 10. The first one occurs at the sample boundary when the ultrasonic pulse goes from the water into the sample. The two fronts between the rubbery and the glassy regions are responsible for the second and the third reflection of the ultrasonic waves. Finally, the fourth echo is observed at the sample boundary on the opposite side of the transducer.

As the two swollen-unswollen fronts moves towards the centre of the sample, the second and third reflection become closer. When these

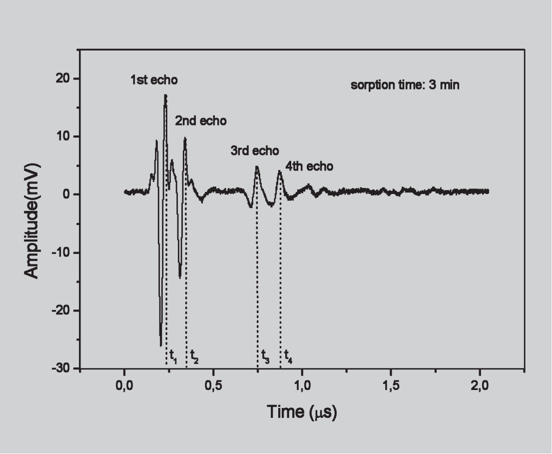


Figure 10 (left): Acoustic signal visualized on the oscilloscope during the water sorption in a PVA sample.

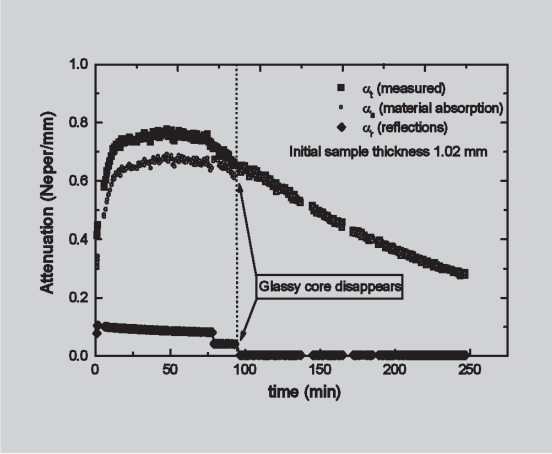


Figure 11: Ultrasonic attenuation for a PVA sample vs. time of water sorption. Comparison of reflections and adsorption contributions to thetotal attenuation.

reflections overlap, the glassy core disappears, indicating that the transition in the rubbery state of the sample is completed and accompanied by a rapid decrease of the attenuation. By monitoring the change of position and amplitude of the detected echoes, it is possible to observe a decrease in the ultrasonic attenuation and longitudinal velocity during water sorption, related to the change of hydrogel density and mechanical properties. In Fig. 11, the different contributions to the total attenuation measured by the pulse-echo technique are reported: the attenuation caused by the absorption, deriving by the molecular relaxation related with the glass transition, and the attenuation caused by reflections at swollen-unswollen fronts.

The ultrasonic technique described above show a strong potential to be applied for studying solvent activated-controlled devices for drug release. In these systems, indeed, the rate of release depends on the swelling kinetics and therefore on the rate of advancement of the glass-rubber front through the hydrogel, which can be reliably monitored by the ultrasonic technique.

5 CONCLUSIONS

In this work, a novel technique for high frequency dynamic mechanical analysis of polymeric materials has been presented. It is based on low intensity ultrasonic waves, propagating through the sample in the MHz range, which assure a fast, non-destructive and non-invasive measurement. Due to the absence on the market of specific instruments, an experimental set-up for generation and detection of ultrasound and for data analysis has been developed. The performance of the new ultrasonic apparatus has been evaluated by monitoring the cross-linking of a thermosetting resin, the crystallization of a semicrystalline polymer and the water sorption process in a dry hydrogel.

The developed instrumentation is able to estimate the viscoelastic properties of polymers and to determine their transition temperatures in a broad temperature range (from -50 to 250 °C), covering the interval of operating temperatures of most common used polymers. The ultrasonic equipment has been fitted into a rotational rheometer in order to superimpose ultrasonic waves with low frequency shear oscillations, leading to a simultaneous dynamic mechanical and ultrasonic experiment and a better insight into the viscoelastic behavior of the tested polymers.

The ultrasonic results presented in this paper are only a few examples of the various applications of this novel experimental set-up, successfully carried out in our laboratory. They demonstrate the reliability of ultrasonic dynamic mechanical analysis in characterizing polymer properties.

REFERENCES

[1] Davis JR et al.: Nondestructive evaluation and quality control, ASM, Metals Park (1992)
[2] Krautkramer J, Krautkramer H: Ultrasoning Testing of Materials, Springer-Verlag, Berlin (1977)
[3] McClements DJ: Advances in the application of ultrasound in food analysis and processing, Trends Food Sci. Techn. 6 (1995) 293-299.
[4] Povey MJW, McClements DJ: Ultrasonics in Food Engineering: Part I. Introduction and Experimental Methods, J. Food Engin. 8 (1988) 217-245.
[5] J. Götz J, Rewesa L, Walch M, Geissler A: Influence of an Ultrasonic Treatment on the Structure and Flow Behaviour of Oxide Ceramic Masses, Appl. Rheol. 15 (2005) 204-217.
[6] Lionetto F, Luprano VAM, Maffezzoli A: Characterization of polymers by ultrasonic dynamic mechanical analysis. In: Recent Research Developments in Applied Polymer Science, Pandalai SG Ed. (2002) 135-156.
[7] Perepechko I: Acoustic Methods of Investigating Polymers, Mir Publishers, Moscow (1975)
[8] Van Krevelen DW: Properties of Polymers, Elsevier, Amsterdam (1990)
[9] Maffezzoli A, Quarta E, Luprano VAM, Montagna G, Nicolais L: Cure monitoring of epoxy matrices for composites by ultrasonic wave propagation, J. Appl. Polym. Sci. 73 (1999) 1969-1977.

[10] Lionetto F, Licciulli A, Montagna F, Maffezzoli A: Piezoceramics: an introductive guide to their practical applications, Ceramurgia/Ceramica Acta (C+CA) 34 (2004) 107-127.

[11] Ferry JD: Viscoelastic Properties of Polymers, John Wiley & Sons, New York (1980)

[12] Lairez D, Durand D, Emery JR: Gelation and vitrification of epoxy resins monitored by ultrasonic measurements, Makromol. Chem. Macromol. Symp. 45 (1991) 31-41.

[13] Alig I, Lellinger D, Johari GP: Relaxations in thermosets. Ultrasonic studies of curing kinetics of ethylene-diamine-cured epoxide, J. Polym. Sci. B: Polym. Phys. 30 (1992) 791-799.

[14] Matsukawa M, Nagai I: Ultrasonic characterization of a polymerizing epoxy resin with imbalanced stoichiometry, J. Acoust. Soc. Am. 99 (1996) 2210-2115.

[15] Frigione M, Maffezzoli A, Acierno D, Luprano VAM, Montagna G: Nondestructive and in-situ monitoring of mechanical property buildup in epoxy adhesives for civil applications by propagation of ultrasonic waves, Polym. Eng. Sci. 40 (2000) 656-664.

[16] Pindinelli C, Montagna G, Luprano VAM, Maffezzoli A: Network development during epoxy curing: Experimental ultrasonic data and theoretical predictions, Macrom. Symp. 180 (2002) 73-88.

[17] Lionetto F, Rizzo R, Luprano VAM, Maffezzoli A: Phase transformations in unsaturated polyester resins during the cure, Mat. Sci. Eng. A 370 (2004) 284-287.

[18] Challis RE, Freemantle RJ, Cocker RP, Chadwick DL, Dare DJ, Martin C, Mahendrasingam A, Fuller W: Ultrasonic measurements related to evolution of structure in curing epoxy resins, Plastics, Rubber and Composites 29 (2000) 109-118.

[19] Challis RE, Unwin ME, Chadwick DL, Freemantle RJ, Partridge IK, Dare DJ, Karkanas PI: Following network formation in an epoxy/amine system by ultrasound, dielectric, and nuclear magnetic resonance measurements: a comparative study, J. Appl. Polym. Sci. 88 (2003) 1665-16753.

[20] Lionetto F, Maffezzoli A: Relaxations during postcure of unsaturated polyester networks by ultrasonic wave propagation, dynamic mechanical and dielectric analysis, J. Polym. Sci. B: Polym. Phys. 43 (2005) 596-602.

[21] Lionetto F, Maffezzoli A, Ottenhof MA, Farhat IA, Mitchell JR: Ultrasonic investigation of wheat starch retrogradation, accepted for publication on J. Food Engin.

[22] Tatibouet J, Pichè L: Ultrasonics Investigation of Semicristalline Polymers: study of Polyethyleneterephtalate, Polymer 32 (1991) 3147-3151.

[23] Gendron R, Tatibouet J, Guevremont J, Dumoulin M M, Pichè L: Ultrasonic behaviour of polymer blends, Polym. Eng. Sci. 35 (1995) 79-91.

[24] Alig I, Tadjbakhsch S: Film Formation and Crystallization Kinetics of Polychloroprene Studied by an Ultrasonic Shear Wave Reflection Method, J. Polym. Sci. B: Polym. Phys. 36 (1998) 2949-2959.

[25] Alig I, Tadjbakhsch S, Floudas G, Tsitsilianis C: Viscoelastic contrast and kinetic frustration during poly(ethylene oxide) crystallization in a homopolymer and tryblock copolymer. Comparison of ultrasonic and low-freqeuncy rheology, Macromol 31 (1998) 6917-6925.

[26] Greco A, Maffezzoli A, Vlachopoulos J: Simulation of heat transfer during rotational molding, Advances in Polymer Technology 22 (2003) 271-279.

[27] McClements D J, Povey M J W, Dickinson E: Absorption and velocity dispersion due to crystallization and melting of emulsion droplets, Ultrasonics 31 (1993) 433–437.

[28] Challis R E, Cocker R P, Holmes A K: The effects of fillers on wide bandwidth ultrasonic pulse propagation in adhesives, Ultrasonics 34 (1996) 355-361.

[29] Maffezzoli A, Tarzia A, Cannoletta D, Montagna G, Luprano VAM: Ultrasonic characterization of the kinetics of water sorption in hydrogels, Macrom. Symp. 138 (1999) 149-155.

[30] Maffezzoli A, Luprano VAM, Montagna G, Esposito F, Nicolais L: Ultrasonic wave attenuation during water sorption in poly(2-hydroxyethyl methacrylate) hydrogels, Polym. Engin. Sci. 36 (1996) 1832-1838.

[31] Maffezzoli A, Luprano VAM, Montagna G, Nicolais L: Ultrasonic characterization of water sorption in poly(2-hydroxyethyl methacrylate) hydrogels, J. Appl. Polym. Sci. 67 (1998) 823-831.