Ultrasonic Dynamic Mechanical Analysis of Polymers

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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

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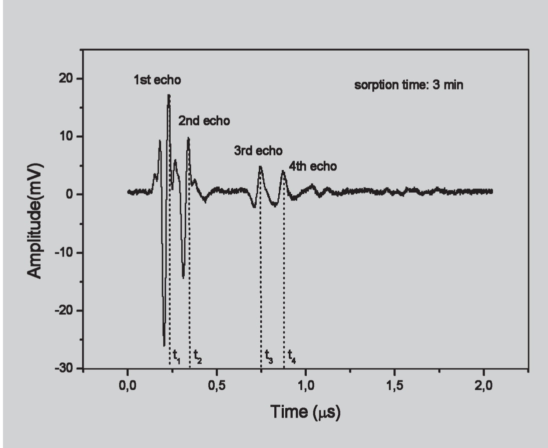
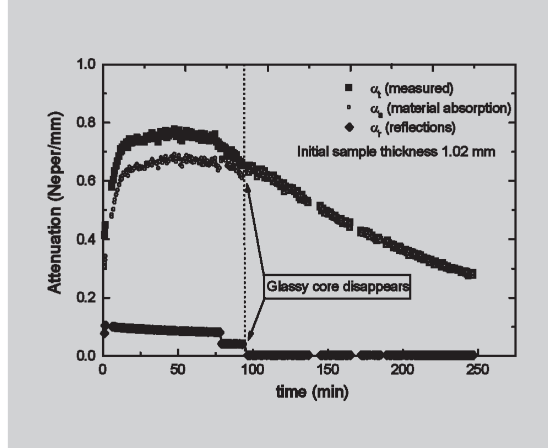
Figure 10 (left): Acoustic signal visualized on the oscilloscope during the water sorption in a PVA sample.

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.

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