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A NEW ULTRASONIC MEASUREMENT SYSTEM FOR THE CURE MONITORING OF THERMOSETTING RESINS AND COMPOSITES

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Abstract

Measurements of the ultrasonic sound speed of thermosetting resins and composites can be used as an in-process cure monitoring technique. Ultrasonic measurements have an advantage over other in-process techniques in that ultrasonic sensors do not make contact with the part (thus leaving no imbedded sensor or witness mark) and can make true bulk measurements of the part. A new commercially available ultrasonic cure monitoring system has been developed which easily enables ultrasonic measurements to be made in compression molding, resin transfer molding, and autoclave processes. Advancements in ultrasonic sensor technology enable the sensor to maintain good coupling to the part during thermal cycling to 260°C. Data is presented showing the change in ultrasonic sound speed during the compression molding of a graphite-epoxy prepreg. The data shows a good relationship to the ionic conductivity and resistivity data collected via dielectric cure monitoring.

Keywords: cure monitoring, thermoset resins/composites, ultrasonic

Introduction

Measurements of the ultrasonic sound speed of thermosetting resins and composites can be correlated to the material's viscosity and cure state. The material under test will change state as it undergoes cure. This change of state can be monitored by measuring the velocity of acoustic waves in the material.

Previously, use of ultrasonic measurements as a cure monitoring technique had been hindered by poor reliability of ultrasonic transducers under typical processing conditions, especially thermal cycling to elevated temperatures. A new in-mold, reusable ultrasonic sensor has been developed. This robust sensor is capable of withstanding hundreds of thermal cycles up to 260°C. Ultrasonic sound speed measurements may now be routinely made during the processing of thermosets using this new sensor technology. An electronics instrumentation and software package has also been developed for the specific application of making a complete ultrasonic cure monitoring system.

The new ultrasonic measurement technology was developed under the National Center for Manufacturing Sciences (NCMS) Adaptive Process Control of Compression Molded Composites Project. The project team members consisted of United

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Technologies, Pratt & Whitney Aircraft; Erie Press Systems; and Allen Bradley, a Rockwell Automation business. Upon successful development and demonstration of the ultrasonic cure monitoring system in a compression molding process by the project team, Micromet Instruments, Inc. became a subcontractor for the project to transfer the technology into a commercially viable sensor and instrumentation system. Micromet Instruments has acquired a license for the ultrasonic sensor system from NCMS and is currently marketing the product it has developed, the UCMS-200 Ultrasonic Cure Monitoring System. Pratt & Whitney and Sikorsky Aircraft are currently evaluating the system for use in controlling the molding of composite parts.

The ultrasonic sensor is located within the mold and does not contact the part. Once the sensor is installed, hundreds of runs can be made with no incremental sensor cost and no lay up of sensors in each part. The ultrasonic technique is ideal for applications where there can be no sensor imbedded in the part or no witness mark on the outside of the part. The system makes a through-transmission measurement which measures the bulk properties of the part, even on thick parts of over 5 cm (2 inches) in thickness. The reusable, non-intrusive nature of the sensor, along with the ability to measure bulk material properties of thick parts, provide unique features over other in-process cure monitoring techniques such as dielectric or fiber optic.

Ultrasonic measurement technique

The ultrasonic measurement system uses piezoelectric elements to generate an acoustic wave. High voltage pulses excite the piezoelectric element in the ultrasonic transducer, causing this element to oscillate at 5 MHz. This creates the acoustic wave that propagates at a material specific velocity. Whenever the wave reaches a boundary some of the wave is transmitted through the boundary into the second material, and some of the wave is reflected back. The transmitted and reflected waves are then collected by the ultrasonic transducers, which also act as ultrasonic sensors. When an acoustic wave reaches the piezoelectric element, the element produces a voltage which is the sensor signal. Measurements of sound velocity by through-transmission require two in-line ultrasonic transducers/sensors. One is used to generate the acoustic pulse while the opposing transducer/sensor records the arrival time of the acoustic wave. The excitation and detection function is alternated between two transducers. The electronics allow for multiple signal averaging thereby creating clean signals. The distance between the opposing sensors is monitored by the system in order to provide accurate distance measurements. The ultrasonic sound speed is then calculated from the time and distance information.

Sensor and sample geometry are critical to this measurement technique. The wave will change direction at a boundary if the wave is not perpendicular to the boundary. Therefore the molds must be carefully machined to insure the required perpendicularity. Holes for the sensors should be 2.54 cm in diameter and bored to within approximately 0.6 cm of the mold inner surface. The bottom surface of the hole must be very smooth to insure good coupling between the piezoelectric element of the sensor and the mold. Silicone grease is used to eliminate any air between these mating surfaces, resulting in good coupling.

Ultrasonic measurement system

The UCMS-200 is a complete stand-alone system consisting of sensors and cabling, a rack-mountable electronics package, and a Windows based LabVIEW software package. A computer is integrated into the electronics package complete with monitor, keyboard, mouse, and disk drives. Figure 1 shows a schematic of the ultrasonic measurement system installed in a compression molding process. An ultrasonic sensor set consists of two sensors located on opposite sides of the mold. For autoclave applications, an ultrasonic sensor is mounted in the tool and the second sensor is mounted in a caul plate which is placed on the sample, beneath the vacuum bag.

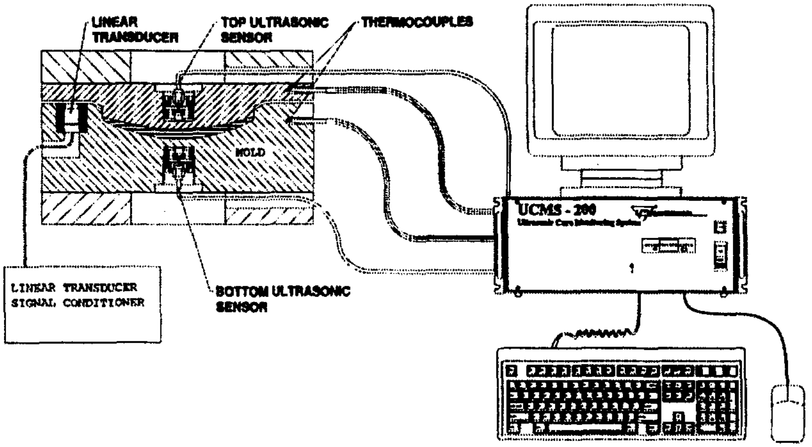

Fig. 1 A schematic representation of the UCMS-200 installed in a compression molding process

The system can measure the ultrasonic sound speed at two different locations using two sets of ultrasonic sensors. Part thickness is monitored using up to four capacitive non-contact displacement probes or linear voltage displacement transducers (LVDT). Accurate measurement of the part thickness is important in accurately calculating the sound speed, especially in processes where the part thickness changes during the cure cycle. Temperature can be measured from two thermocouples.

The LabVIEW based software package enables easy operation of the system and allows the display screen to be customized by the user. Algorithms can be easily written by the user to perform special functions and closed loop control of the process.

Experimental results

The change in sound speed has been correlated with the change in the viscosity of the prepreg [1]. Heating the prepreg decreases the material's viscosity and the acoustic wave velocity is decreased. As the material cures, the molecular structure is constrained and supports a higher acoustic wave velocity. The change in ultrasonic sound speed of an epoxy-graphite fiber prepreg during a compression molding process is plotted in Fig. 2. The initial decrease in sound speed shows the decrease in viscosity as the prepreg increases in temperature. A broad minimum is seen as the temperature cycle enters a 121°C hold period. As the temperature is increased to 177°C, the sound speed increases as curing causes the viscosity of the prepreg to increase. The rate of increase in sound speed then slows as the rate of cure slows and the reaction nears completion.

Dielectric cure monitoring is a widely used, in-process cure monitoring technique involving the measurement of changes in the electrical conductivity of the material. Dielectric measurements have been shown to correlate with the change in viscosity and cure state of epoxy and other thermosetting resins and composites [2–4]. Dielectric cure monitoring data thus provide a good comparator to the validity of the ultrasonic sound speed in the cure monitoring. Figure 3 compares the ionic conductivity as measured by a Micromet Instruments Eumetric System II Microdielectrometer to the ultrasonic sound speed of an epoxy-graphite fiber prepreg [1]. The ultrasonic sound speed exhibits a good inverse relationship to the log conductivity data. This inverse relationship is expected since ionic motion is reduced with higher cross-linking of the material, whereas the velocity of the acoustic wave is increased.

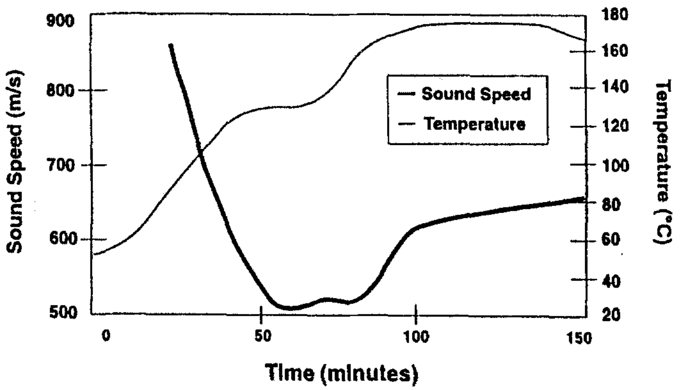

Fig. 2 The change in ultrasonic sound speed and temperature of an epoxy-graphite fiber prepreg during a compression molding process

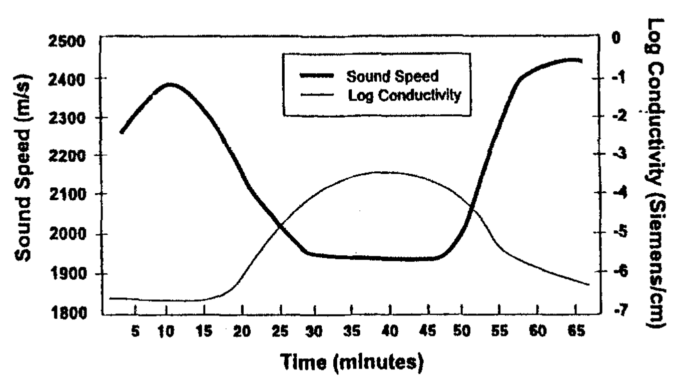

Fig. 3 A comparison of the ultrasonic sound speed with the ionic conductivity during the compression molding of an epoxy-graphite fiber prepreg

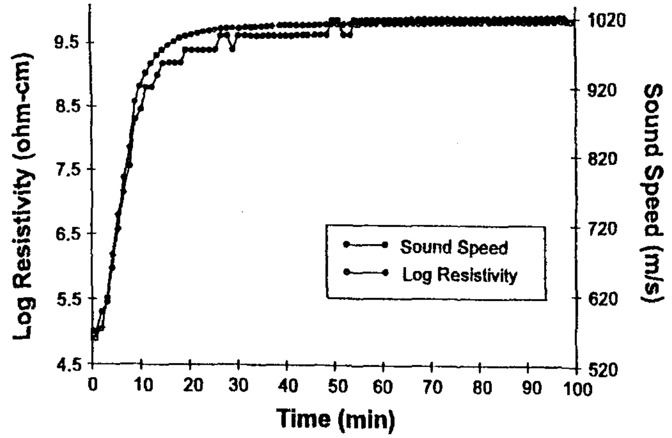

Fig. 4 Isothermal cure of epoxy glass composite

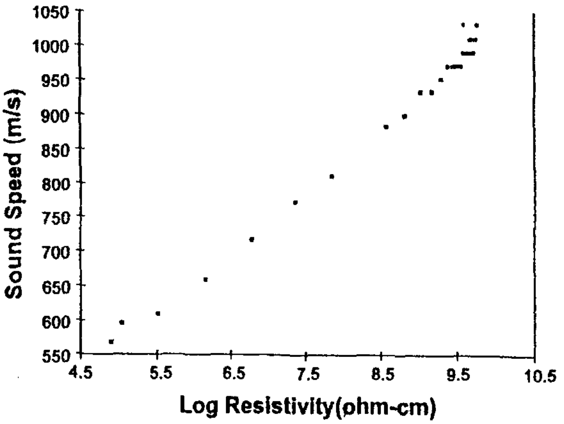

Fig. 5 Cross plot of sound speed *vs.* log resistivity

Since the sound speed is inversely related to the log conductivity, a plot of the log resistivity (1/log conductivity) should closely track the sound speed. Figure 4 compares the ultrasonic sound speed and log resistivity during the 150°C isothermal cure of a 2.3 mm thick epoxy-glass fiber prepreg. The sound speed and log resisitivity data were measured simultaneously in a compression mold and show an excellent correlation between the two curves. The apparent step function in the sound speed data is the limit of resolution of the time of flight through such a thin sample. On thicker samples, the sound speed resolution will increase, thus increasing the sensitivity of the data to the end of cure.

The excellent correlation of the sound speed to log resistivity can be seen in Fig. 5 where the sound speed is plotted as a function of log resistivity during the 150°C isothermal cure of the glass-epoxy prepreg. A near linear relationship is observed until the sound speed increases above a level of 900 m s^{-1}. After this point, the quantification of the sound speed data prohibits a valid assessment of the relative sensitivity of the two measurement techniques to the end of cure.

Future work

Work is currently under way to redesign the ultrasonic sensor so that it may be more easily installed in the mold by the user. In the current sensor design, the sensor must be assembled by individually installing the components into the sensor cavity in the mold. The sensor must then be tuned by tightening the sensor until a good pulse/echo response is obtained. The re-designed sensor will be of a "Plug-In" design where the sensor components will be pre-installed within the sensor housing and tuned. The sensor will then be screwed into the sensor cavity and tightened to a preset level using a torque wrench.

Future applications work will concentrate on resin systems where reaction by-products prevent dielectric cure monitoring from providing useful data, such as phenolic resins. Thicker samples of epoxy prepreg will be cured to more accurately compare the sensitivity to the end of cure of the ultrasonic sound speed with the log resistivity.

Conclusions

A new commercially available ultrasonic cure monitoring system has been developed which enables ultrasonic measurements to be easily made during the processing of thermosets in presses, autoclaves, and RTM processes. New ultrasonic sensors maintain good coupling to the mold during thermal cycling to 260°C. The non-intrusive ultrasonic sensors do not contact the part and thus leave no mark on the part or sensor embedded in the part. The ultrasonic measurements provide a bulk measurement which correlates with the change in material viscosity and correlates well with dielectric cure monitoring data. The ultrasonic cure monitoring system can be used for production closed-loop control of thermoset composite processing.

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