COMBINING WAVE AND SPECTROSCOPIC TECHNIQUES TO MONITOR THE DEVELOPMENT OF THERMOSETS DURING CURE

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Abstract

This work presents the first attempt to use ultrasonic sensors and a Raman spectrometer in a single testing set-up. The aim is to evaluate methods to infer thermo-chemical and mechanical properties of thermosets in one experiment. Basics of both technologies are outlined. On this basis a measurement device is presented as a proof of concept to test thermosetting sytems under isothermal conditions. The Raman data processing algorithm BEADS is implemented and the signal analysis regarding the degree of cure is described. To validate this new technique, three epoxy systems are tested. Preliminary results of the prototype show general agreement between Raman results and standard DSC testing. The results show the necessity of further development of the algorithm. Ultrasound results of the time of flight of longitudinal waves through epoxy samples is as expected, with sensor limitations for high temperature measurements.

1. Introduction

The use of fiber reinforced thermosets (FRT), due to their lightweight properties, continues increasing in high volume industries like the automotive industry. One topic preventing the wider spread of FRT in these industries is the complex warpage behavior due to curing. The development of the mechanical properties with the degree of cure is one of the factors that causes warpage. In order to predict this part distortions, efforts have been made to characterize the cure dependent properties of the resin. The accuracy of the constitutive models used in simulations defines the quality of the simulations/predictions, and those models rely heavily on the available data. Most thermosetting characterization procedures involve laborious testing with multiple devices. Furthermore, most methods determine properties at discrete points of temperature and/or cure history. Continuous measurements of multiple properties save characterization time and offer the opportunity to enhance the understanding of the cure dependent changes in thermosets and the corresponding composites.

The combination of ultrasound and Raman spectroscopy will be investigated as a possibility for measuring the degree of cure and mechanical properties simultaneously. This method is compared to established means of thermosetting cure characterization, such as Differential Scanning Calorimetry (DSC).

Ultrasound wave propagation has been reported as a tool to measure mechanical properties since 1948 [1]. In 2008, McHugh reported ultrasound as a high frequency DMA technique for polymer characterization [2]. McHugh suggested the need of combining wave analysis with kinetic models for cure prediction [2]. Ultrasound wave propagation has also been used for cure monitoring [3-6], online process monitoring of polymer composites production [7], and as in-situ non-invasive mechanical characterization [8].

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Ultrasound is used in the composites industry as a non-destructive testing (NDT) method to quantify material properties and to evaluate material microstructure. The ultrasound signal is used to control porosity, voids, and to predict cracks or defects in parts. Additionally, ultrasound wave propagation can be used to infer mechanical properties of materials, including the elastic modulus, shear modulus and viscous damping. Raman spectroscopy on the other hand has been used as a cure characterization tool. In 2008, Cruz showed the advantages of Raman spectroscopy over DSC in the characterization of thermosets [9].

This work presents the development of an apparatus to monitor thermosetting resins combining a Raman-spectroscope and ultrasonic sensors. The target is the degree of cure and its relationship with mechanical property development of thermosets during cure. The apparatus consists of a heated measuring chamber that allows isothermal and dynamic curing conditions. The Raman-spectroscope enables the quantification of frequency changes in the molecules (vibrations, rotations, etc), and the ultrasonic sensors quantify the time of flight of sound waves through the material as it cures. Both measurements together can allow the correlation of the degree of cure with the mechanical property development of the material. Three epoxy resins are measured by DSC and by the proposed approach. The results are compared and the accuracy of the new approach is evaluated.

2. Fundamentals

Ultrasound wave propagation makes use of a piezoelectric disc to convert an electrical signal into a mechanical signal. Piezoelectric materials can be polarized in a particular direction. As a consequence, when an electrical signal is applied the material undergoes a small change in length in the polarized direction. A couplant agent in the interface between the piezoelectric material and the test specimen allows the transfer of energy to the sample. The frecuencies of ultrasound measurements range between 1 and 20 MHz. The waves generated by the piezoelectric transducers travel through the sample at the speed of sound. The speed of sound changes based on the stiffness of the material.

Ultrasonic waves attenuate as they travel through the medium of interest. Thermosets attenuate ultrasonic waves rapidly due to their viscoelastic nature. In ultrasound wave propagation, there is a trade off beween achieving a better resolution at higher frequencies with the consequence of experiencing more attenuation. Dynamic mechanical properties of viscoelastic materials are inferred from the knowledge of the speed of sound and attenuation. The calculation of the speed of sound in thermosets involves the accurate quantification of thickness changes due to chemical shrinkage and thermal expansion.

The Raman effect refers to the inelastic scattering of radiation by chemical bonds. The energy shift of the scattered photons can be directly correlated to a specific bond and is independent of the incoming photon's energy [10]. The intensity of Raman scattered photons depends directly on the number of bonds in the evaluated volume [11]. Therefore, changes in the chemical constitution can be monitored directly. Due to energetic considerations energy shifts to lower frequencies are much more likely than upshifts. Raman lines are usually reported in wavenumbers, being the inverse of wavelengths.

3. Experimental

3.1 Materials

Three epoxy systems were tested in this study.The first material tested was system 2000 epoxy resin mixed with hardener 2020 both from Fibre Glast Development Corporation. Epoxy 2000 is a mixed activated themoset that cures at room temperature, it is used as a bonding matrix of a fiber reinforcement for structural applications. The next two materials tested were epoxy film adhesives DA 408 and 409 from Adhesive Prepregs for Composite Manufacturers (A.P.C.M. LLC). Both epoxies are heat activated systems used in bonding of composites and as the matrix of unidirectional carbon fiber prepregs.

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3.2 Apparatus

The device presented here is a measurement chamber that incorporates a Raman spectrometer and ultrasound transducers. This design addresses the simultaneous curing characterization and mechanical development of thermosets. The device features a mold-plunger design to follow the cure dependency of the pvT behavior in thermosets, comparable to the PVT-α by Nawab *et al*. and other equivalent dilatometric devices [10]. Figure 1 shows a schematic sectional view of the mold.

The mold cavity holds a 78 mm in diameter and 3.5 mm thick disk specimen, and it has a demolding angle of 3°. The energy input is a heating band placed around the mold. The plunger has a flange where six screws, each equipped with a spring, provide a constant pressure to compensate for the chemical shrinkage of the specimen. A counterbore hole sealed by a quartz disk allows the Raman-spectrometer laser to reach the sample at a constant distance. Two ultrasound transducers (transmitter and receiver) are placed facing each other in the flat surface of the mold cavity and the plunger in order to perform a measurement. The transducers are aligned symmetrically to the Raman cavity in order to test the same curing conditions.The temperature profiles in the mold cavity and plunger are controlled by a PID-controller in combination with a thermocouple located in the mold's center hole.

The wave propagation setup consists of a set of ultrasonic transducers, a Panametrics pulser-receiver (Model 500RP), and an oscilloscope (Singlent SDS 1052DL). Two pairs of transducers are used, longitudinal wave transducer, 1 MHz (Panametrics Model V102), and shear wave transducer, 1 MHz (Panametrics Model V153). These ultrasound transducers lose their piezoelectric properties above 50°C; based on the work of Ko *et al.* [11], delay lines are used to insulate the transducers during testing (6.35 mm thick quartz). The Raman unit is composed of a HyperFlux U1 Spectrometer with an Andor iDus DU416A-LDC-CCD by Tornado Spectral Systems, Ithaca, NY and an RFP-400 probe by Hellma Axiom, Inc., Tustin, CA. The laser wavelength used is 785 nm.

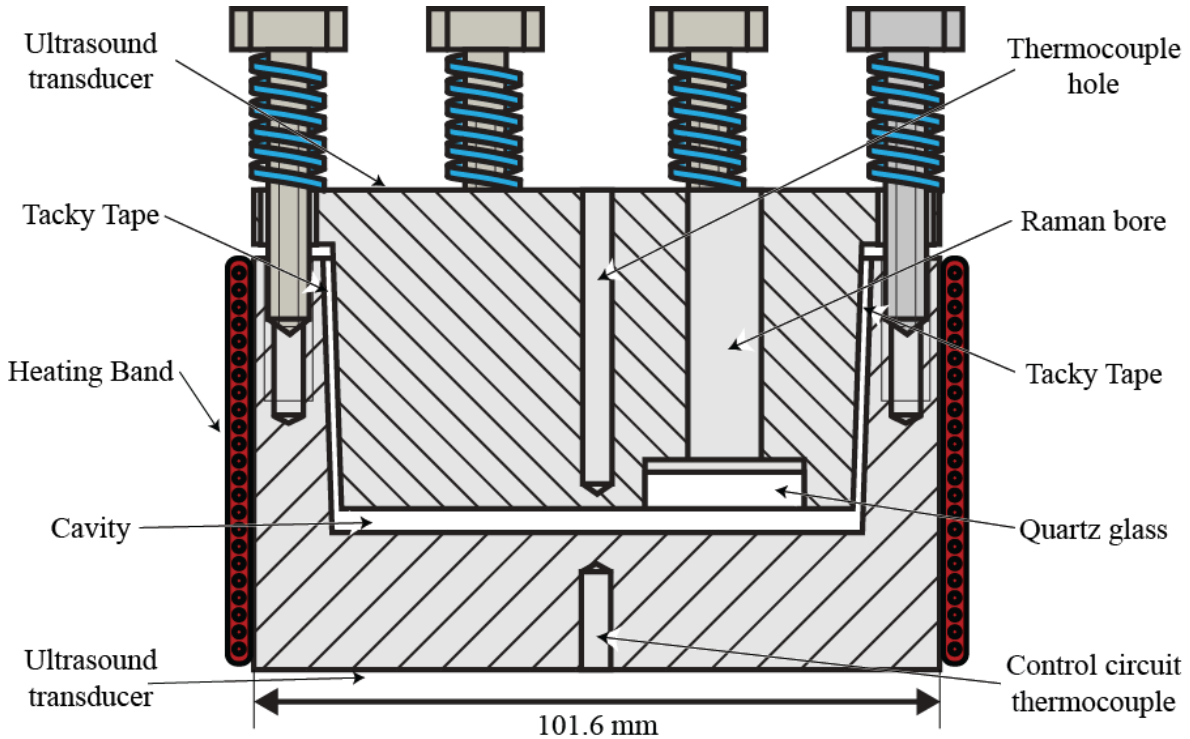

Figure 1. Sectional view of measurement device

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3.3 Methods

Ultrasound measurements are taken by placing the sensors with the delay lines on the mold for a period of 5 s. After the data is collected the sensors are removed and the delay lines cool down for the next measurement. This process is repeated every three minutes avoiding transducer overheating and corruption of the piezoelectric signal. Glycerol 96% is used as the couplant agent.

The measured ultrasound signal includes the information of all the different materials placed in between the transducers. To extract the data corresponding to the epoxy specimen, the superposed time of flight and attenuation of the aluminum, the glass delay lines and the couplant agent are substracted from the original signal. For this calibration, the temperature dependency of the aluminum is measured from 20°C to 120°C in increments of 20°C as seen in Table 1. The quartz disks are only characterized at room temperature neglecting the small temperature effects in the 5 s interval.

Table 1. Time of flight (t_{of}) of ultrasound through device components

Temperature (°C)	t_{of} plunger (µs)	t_{of} plunger & glass (µs)	t_{of} complete (µs)
20	7.5	9.70	12.92
40		9.76	13.00
60		9.80	13.06
80		9.84	13.12
90		9.88	13.18

The Raman settings for the three epoxies of study are a laser power of 400 mV, and an exposure time of 2000 µs with an averaging of 10 measurements for each data point. The original measured spectral signal includes background and noise. To extract the Raman signal, the "Baseline Estimation and Denoising with Sparsity (BEADS)" proposed by *Ning et al* [12] is applied to every measured signal. This algorithm models the Raman signal as sparse peaks and optimizes their shape by comparing it to the original signal while using a high and low pass filter for the separation of the noise and baseline, respectively.

To compare different spectra intensities, every spectrum is normalized by a peak that would not ungergo changes due to the curing reaction [13]. Peak 1188 cm^{-1}, that corresponds to the CH- backbone vibration, is used for the three materials of study. This peak is commonly used as the normalization peak in epoxy systems, because the number of elements is not affected by the reaction [13,14]. A slight shift of the peak was recognized in the data, therefore the BEADS algorithm is modified to determine the maximum value in a narrow range (+/- 5 data points) around the original peak and to average it with the data point before and after to compensate for shape changes. Equation 1 shows the averaging process for peak 1188 cm^{-1} with *I(wn)* being the peak intensity value and *wn* the variable for the wavenumbers.

$$\bar{I}(wn) = \frac{3 * I(wn)}{\sum_{i=-1}^{1} I_{i=0}^{max}(1188\ 1/cm)} \quad (1)$$

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By normalizing the data, different measurements can be comparatively evaluated regarding the degree of cure $\boldsymbol{C}^*$. From 200 cm^{-1} up to 4000 cm^{-1} several peaks show changes based on the progression of the curing reaction [9]. Here peak 1255 cm^{-1} that corresponds to the oxirane vibration is evaluated. To compensate for the temperature dependent broadening effects of this peak [15], a cumulative peak intensity $\boldsymbol{A}(\boldsymbol{I}(\mathbf{1255}^{+/-}\mathbf{5}\ \boldsymbol{cm}^{-\mathbf{1}})$ is used. Equation 2 represents the definition of degree of cure in the Raman analysis, with $\boldsymbol{A_o}$ and $\boldsymbol{A}_\infty$ being the normalized peak intensity of the uncured and fully cured material respectively.

$$C^*(t) = \frac{A_o - A(t)}{A_0 - A_\infty} \tag{2}$$

A_∞ is determined from measurements of fully cured specimens. The determination of A_o depends on the epoxy system. For the adhesives DA 408 and DA 409 a sample is removed from the freezer and A_o is determined from a measurement at room temperature without any heat treatment. The curing reaction during the storage and testing protocol is neglected in the analysis. In contrast, the signal for A_o of system epoxy 2000 is compounded from separate measurements of the epoxy 2000 and the hardener 2020 accordingly to the mix ratio [14].

4. Results

4.1 Mixed activated resin

The initial design of the measurement chamber shows the potential to follow the curing reaction and the evolution of the mechanical properties simultaneously. Figures 2 (a)-(c) show the change in degree of cure for the 2000 epoxy resin system as a function of time at three different curing temperatures. The data's time signature is referenced to the start of the temperature cycle. No data is available for the time necessary for mixing, degassing and mold assembly. Figures 2 (b)-(c) show vertical shifts of the degree of cure, which are due to the BEADS algorithm's strong sensitivity to the definition of $\boldsymbol{A_o}$. The shifting error for Figure 2 (a) is corrected, as $\boldsymbol{A}_\infty$ is determined by the last five data points of each of the displayed data sets. Based on the work of *Musto et al.* on the general applicability of the composed signal of two separate materials [14], the Raman results are in general agreement with the DSC results with a slight vertical shift.

The time of flight of the longitudinal waves through the epoxy resin is displayed inversely in Figure 3. The displayed values correlate directly to the speed of sound and therefore the mechanical properties of the material. The material shows the expected behavior with a significant increase in the first 20 min of testing, when the majority of the reaction takes place. In contrast to the degree of cure information, the time of flight results indicate ongoing changes in the material. This point agrees with the observation, that the specimen sticks to the plunger after demolding and uncured resin is found on the mold side of the specimen. The amplitude data obtained is not conclusive, due to too long testing intervals and also the amplitude's strong dependency on the pressure applied on the transducers. Further iterations involve the tuning of the protocol to accurately capture attenuation.

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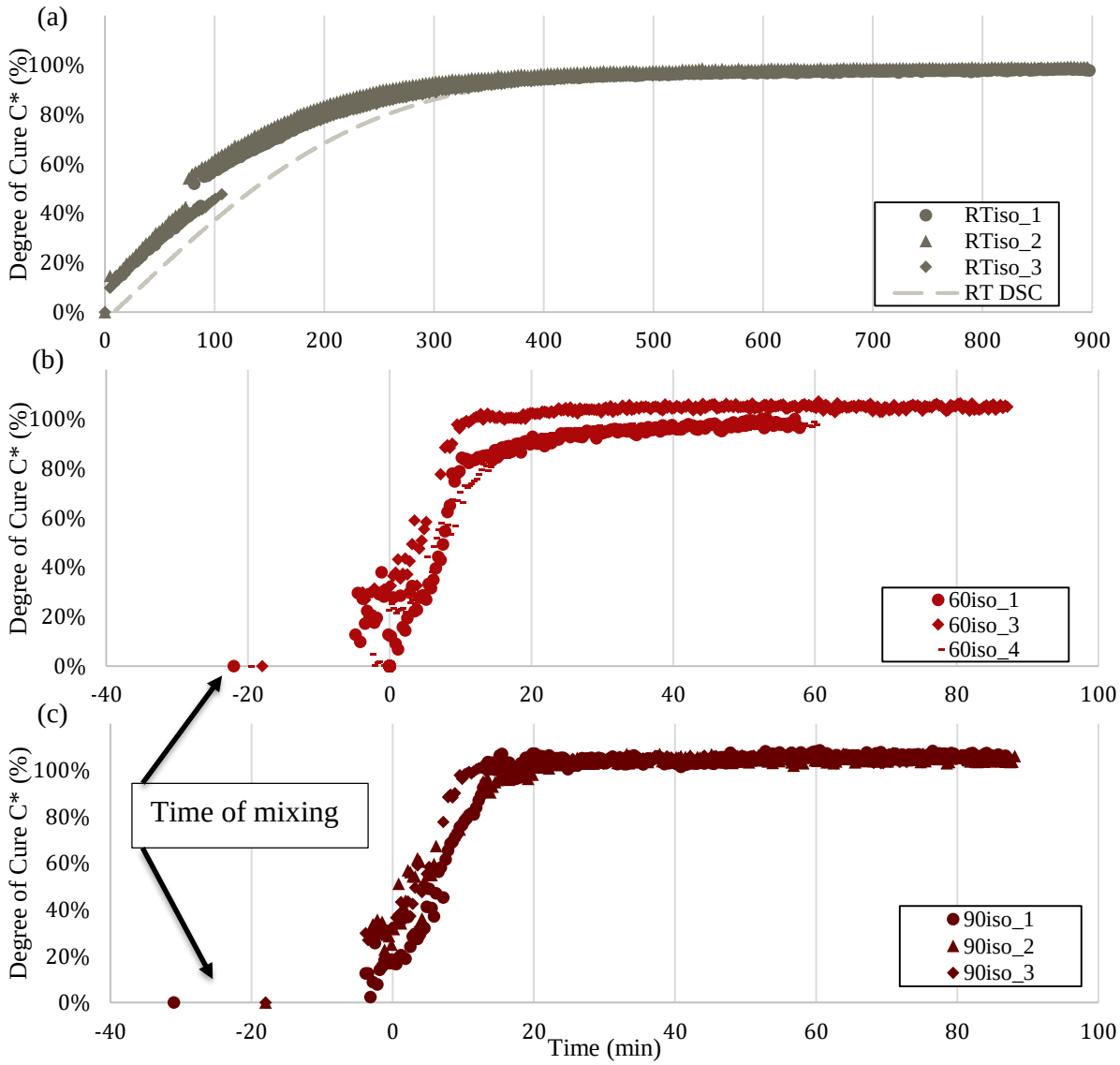

Figure 2. Plots of the Degree of Cure over time at (a) room temperature, (b) 60°C and (c) 90°

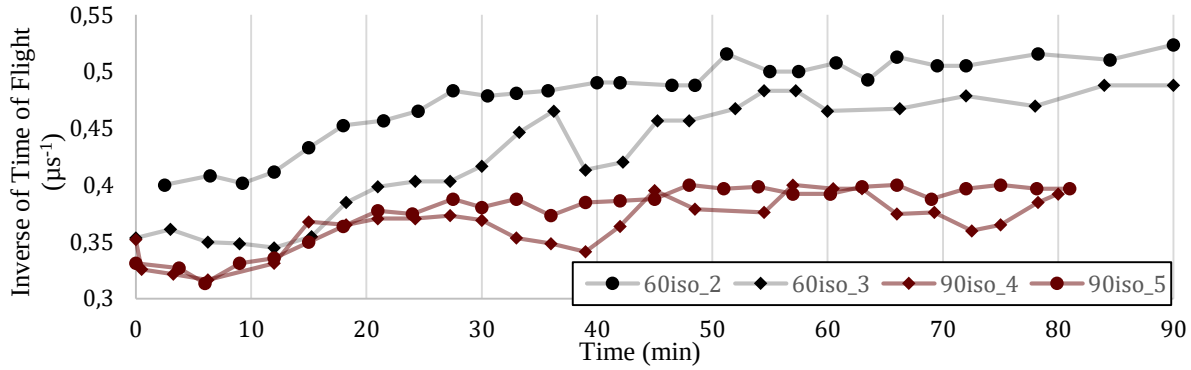

Figure 3. Plot of the inverse time of flight over time for different isothermal holding temperatures

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4.2 Heat activated adhesives

A processing temperature of 120°C is used for epoxy resins DA 408 and DA 409 to enable shorter testing cycles. The temperature increment has a significant effect on the degree of cure for the epoxy adhesive 408, which cures in a shorter time, as shown in Figure 4. The use of a higher temperature reduces testing time but challenges the data processing more. The degree of cure determined by Raman follows the one determined via DSC, but strong scattering of the data points is obvious. Therefore, further iterations require the study of the temperature influence on the peaks height and width, to accurately postprocess the signal in the beads algorithm.

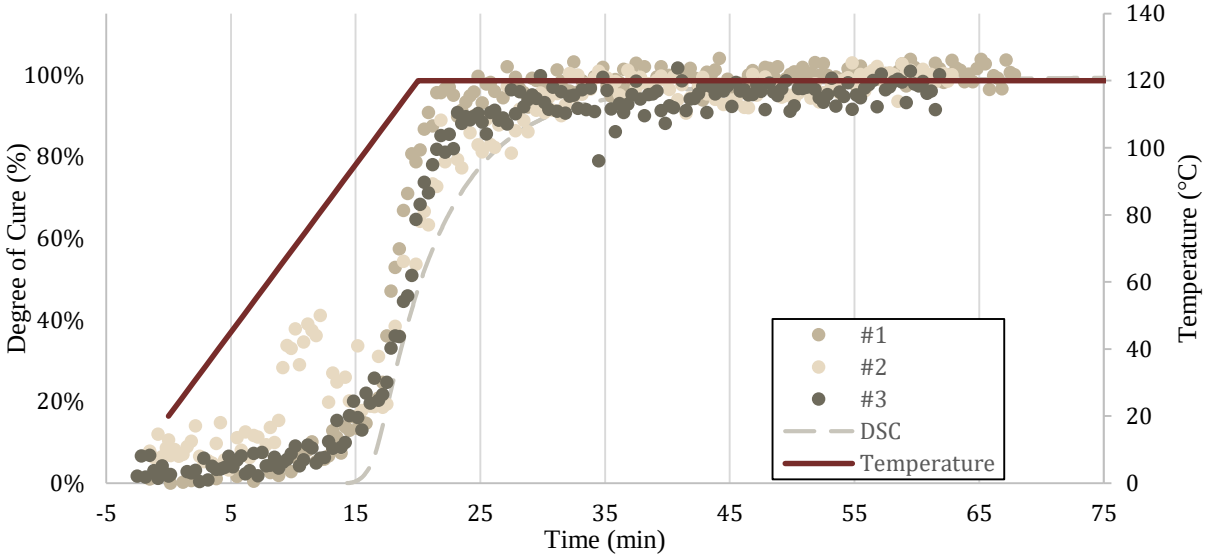

Figure 4. Plot of the Degree of Cure over time for epoxy DA 408.

The curing behavior of the epoxy DA 409 can be obtained very accurately by Raman as seen in Figure 5. The Raman measurement data displays good agreement to the DSC data, but the values its values are higher than the DSC ones, which is also reported by *Cruz* and explained by following the actual chemical reaction [9]. During the initial period of the reaction there is a difference in the conversion values compared to DSC because Raman is monitoring the real conversion process [9].

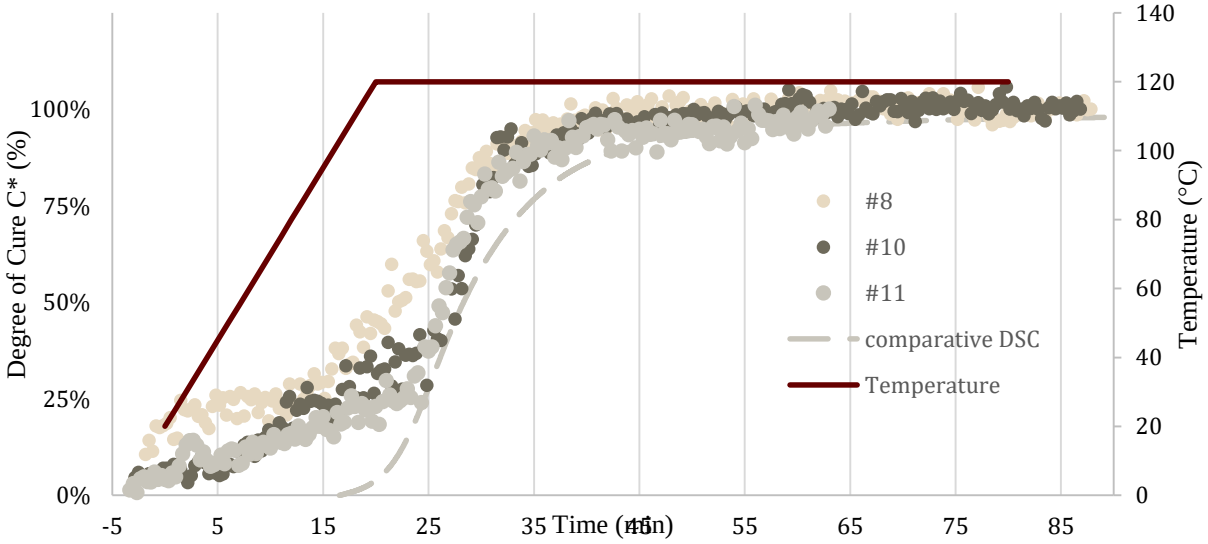

Figure 5. Plot of the Degree of Cure over time for the EP 409 material

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Ultrasound measurements are also performed for epoxy films DA 408 and DA 409. For both materials signal is captured for the intial and end stages of the reaction. At the time, when the majority of the reaction happens according to Raman and DSC, no ultrasound signal is detected. Krautkämper *et al.* explain this phenomena as a result of high testing temperatures and the exothermal heat generated due to the reaction [18]. With low temperature transducers, the signals before and after the majority of the reaction can be obtained and are still valuable information in terms of assessing duration of a process. However the current test setup and equipment prevent the possibility to capture the stage when the sharp increase of the reaction occurs in heat activated systems, whereas suitable transducers are commercially available.

5. Conclusions

The simultaneous use of Raman spectroscopy and ultrasound wave propagation shows promising initial results for advancing the understanding of the degree of cure's influence on the mechanical properties' development as the material shrinks and undergoes phase changes. Because the inavailability of high temperature stable ultrasound sensors, it can be seen as a proof of concept. The implementation of ultrasound transducers designed for low temperature in heat activated systems is feasible, but restricted by the high attenuation presented during the exothermal reselase of energy.

The degree of cure can be monitored temperature dependent by the Raman setup. Although the evalution algorithm is generally capable, it needs to be stated, that refinement is necessary. It was observed that temperature causes changes in height and width of the evaluated peaks [9, 15], which is a topic for further study.

The next step is to integrate Raman and/or ultrasound in a measurement device similar to the PVT-α, with temperature-stable ultrasound sensors and displacement measurement devices.

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7. References

[1] A. W. Nolle, "Methods for Measuring Dynamic Mechanical Properties of Rubber- Like Materials," *J. Appl. Phys.*, vol. 19, no. 8, pp. 753–774, Aug. 1948.
[2] J. McHugh, "Ultrasound Technique for the Dynamic Mechanical Analysis (DMA) of Polymers," PhD thesis, Technical University of Berlin, Berlin, Germany, 2008.
[3] A. Maffezzoli, E. Quarta, V. a. M. Luprano, G. Montagna, and L. Nicolais, "Cure monitoring of epoxy matrices for composites by ultrasonic wave propagation," *J. Appl. Polym. Sci.*, vol. 73, no. 10, pp. 1969–1977, Sep. 1999.
[4] F. Lionetto, F. Montagna, and A. Maffezzoli, "Ultrasonic dynamic mechanical analysis of polymers," *Appl. Rheol.*, vol. 15, no. 5, pp. 326–335, 2005.
[5] F. Lionetto and A. Maffezzoli, "Monitoring the cure state of thermosetting resins by ultrasound," *Materials*, vol. 6, no. 9, pp. 3783–3804, 2013.
[6] Döring, J., Bartush, J., McHugh, J., and Stark, W., "Contribution to Ultrasound Cure Control for Composite Manufacturing," presented at the 15th World Conference on Nondestructive Testing, Roma (Italy), 2000.
[7] R. Meier, S. Zaremba, F. Springl, K. Drechsler, F. Gaille, and C. Weimer, "ONLINE PROCESS MONITORING SYSTEMS–BENCHMARK AND TEST STUDY," in *Flow Processes in Composites Materials-11*, Auckland, New Zeland, 2012.

Excerpt from ISBN 978-3-00-053387-7

[8] M. Frigione, A. Maffezzoli, D. Acierno, V. a. M. Luprano, and G. Montagna, "Nondestructive and in-situ monitoring of mechanical property buildup in epoxy adhesives for civil applications by propagation of ultrasonic waves," *Polym. Eng. Sci.*, vol. 40, no. 3, pp. 656–664, Mar. 2000.
[9] Javier C. Cruz, "Advanced Cure Monitoring and Analysis for Optimization of Thermoset Resin Processes," PhD thesis, UW Madison, 2008.
[10] I. V. Hertel and C.-P. Schulz, *Atome, Moleküle und optische Physik 2: Moleküle und Photonen - Spektroskopie und Streuphysik*. Springer Berlin Heidelberg, 2010.
[11] L. D. S. Yadav, *Organic Spectroscopy*. Springer Science & Business Media, 2005.
[12] Y. Nawab, S. Shahid, N. Boyard, and F. Jacquemin, "Chemical shrinkage characterization techniques for thermoset resins and associated composites," *J. Mater. Sci.*, vol. 48, no. 16, pp. 5387–5409, Apr. 2013.
[13] R. T. Ko, C. W. Lee, T. Storage, and M. Y. Chen, "Ultrasonic measurements of polyimide materials during heating," in *AIP Conference Proceedings*, 2012, vol. 1430, pp. 1699–1706.
[14] X. Ning, I. W. Selesnick, and L. Duval, "Chromatogram baseline estimation and denoising using sparsity (BEADS)," *Chemom. Intell. Lab. Syst.*, vol. 139, pp. 156–167, Dec. 2014.
[15] J. C. Cruz and T. A. Osswald, "Monitoring epoxy and unsaturated polyester reactions under pressure—Reaction rates and mechanical properties," *Polym. Eng. Sci.*, vol. 49, no. 11, pp. 2099–2108, Nov. 2009.
[16] P. Musto, M. Abbate, G. Ragosta, and G. Scarinzi, "A study by Raman, near-infrared and dynamic-mechanical spectroscopies on the curing behaviour, molecular structure and viscoelastic properties of epoxy/anhydride networks," *Polymer*, vol. 48, no. 13, pp. 3703–3716, Jun. 2007.
[17] V. Janarthanan and G. Thyagarajan, "Temperature and radiation effects on the Raman bands of epoxy resin," *J. Chem. Sci.*, vol. 102, no. 5, pp. 721–723, Oct. 1990.
[18] D. rer nat D.-I. E. h J. Krautkrämer and D. rer nat H. Krautkrämer, "Testing Problems on Non-metallic Specimens," in *Ultrasonic Testing of Materials*, Springer Berlin Heidelberg, 1990, pp. 514–527.

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