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In-Situ Investigation of Resin Shrinkage in the Composite Manufacturing Environment

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Abstract
Cure shrinkage of the polymer matrix during the composite manufacturing process leads to residual stresses, which can adversely affect the structural integrity and dimensional stability of composite structures. In this paper, a novel approach is developed for measuring the resin shrinkage and strain evolution of an epoxy resin (EPON-862) in the composite manufacturing environment. The resin is cured in a custom designed autoclave with borosilicate viewports, while digital image correlation (DIC) is used to analyze the strain evolution throughout the cure cycle. These processing induced strains are correlated to the cure-state using differential scanning calorimetery (DSC). The different mechanisms involved in the polymer strain evolution during composite processing are discussed.

Keywords Digital Image Correlation (DIC) · Autoclave · Differential Scanning Calorimeter (DSC) · Degree of cure

1 Introduction

The curing of polymers during composite processing comprises close packing of molecules through polymerization, which leads to a bulk contraction known as cure-shrinkage [1]. Processing induced strains can cause defects such as matrix cracking, delamination and warpage during composite manufacturing [2]. Many experimental approaches have been developed to evaluate the cure shrinkage. These include dilatometric methods based on measuring the volume change [3] and non-dilatometric methods like rheometry [4]. While these approaches are effective for evaluating polymer behavior in laboratory conditions, an in-situ approach in the manufacturing environment of composite structures is required to understand how resin shrinkage affects composite processing. High-quality composite structures are commonly manufactured in autoclaves at high temperature and pressure. In this paper, an in-situ approach is developed for analyzing cure shrinkage using a Digital Image Correlation (DIC) through glass-viewports of a custom designed autoclave.

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DIC is a non-contact optical technique that monitors the movement of speckle patterns on the surface of interest to generate continuous three-dimensional displacement and strain profiles. In a recent study, Kravchenko et al. [5] used a DIC method to measure in-plane polymer shrinkage to analyze the stress-free strain field for an out-of-autoclave epoxy resin system. Here, this approach is extended to 3D measurements and to the autoclave manufacturing environment. The in-situ measurements of cure-induced deformations are then correlated with the degree-of-cure analyzed using Differential Scanning Calorimetry (DSC). The objective of the paper is to develop a new in-situ method to measure cure shrinkage of polymers in the composites manufacturing environment and correlate it to the cure kinetics.

2 Experimental

A commonly used Epoxy Bisphenol F resin EPON-862 with Diethyl Toulene Diamine (DETDA) as curing agent produced by Hexion is used in this study. DETDA is an aromatic amine hardener that does not contain carcinogenic methylene dianiline. The manufacturing data sheet specifies EPON-862: DETDA weight ratio of 100:26.4 and a glass-transition-temperature in the range of 134–156 °C [6].

2.1 In-Situ Characterization

A custom autoclave equipped with borosilicate-glass viewports, instrumented with a DIC as shown schematically in Fig. 1b, is utilized for the in-situ experiments. A 15×7 cm^2 region is sealed off on a flat aluminum plate using sealant tape to create a container to hold the resin. The EPON-862 resin and DETDA hardener with the weight ratio of 100:26.9 are mixed thoroughly and poured into the container. A thin peel ply with a printed speckle

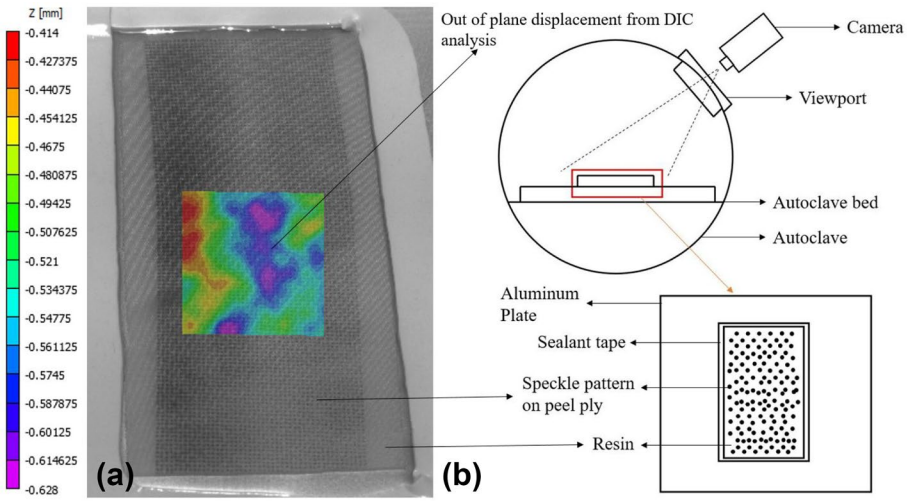

Fig. 1 **a** Out of plane displacement profile for the Epon-862 sample at the end of cure, **b** Schematic of the experimental setup

pattern is placed on the resin. The samples are then cured in the autoclave at three different temperatures (120 °C, 150 °C and 177 °C). During the initial experiment, the airflow in the autoclave caused the additional movement in the resin sample. Two aluminum plates were used to avoid direct airflow to the resin sample to minimize this effect. The crosslinking and thermal deformation in the resin sample lead to a relative change in the speckle pattern position, which allows for the in-situ measurement of displacements and strains using the digital image correlation.

The VIC-3D Real-Time DIC System from Correlated Solutions used for the in-situ analysis consists of two 6-megapixel high-resolution monochromatic cameras. DIC works by tracking the changes in the gray value pattern of the surface marked with a fine random speckle pattern. The speckle pattern could not be directly deposited on the liquid resin; therefore, it is painted on to a thin peel-ply (0.11 mm thickness) and placed on top of the resin sample. The peel-ply stiffness is assumed to be small compared to that of the resin sample at the gelation due to the significant difference in the thickness of the resin sample (2.54 mm) and the peel-ply. Digital images of the surface of the resin sample are captured every 60 s throughout the cure cycle. The first image is considered to be the reference image. The VIC-3D software associated with the DIC calculates the displacement field by matching the speckle pattern on a deformed specimen with that of the reference image. Since it is impossible to find the matched speckle point in a single pixel, an area with multiple pixel points (such as 20x20 pixels) is used to perform the matching process [7]. This area is usually called a subset, and by tracking these subsets, the system can measure in-plane and out-of-plane displacement vector fields and strain maps. The system accuracy for out of plane measurements is 0.04 pixels [8], and the uncertainty for a typical speckle pattern used here is 0.006 pixels.

2.2 Thermal Analysis

DSC-3 differential scanning calorimeter by Mettler Toledo is used to measure the heat of reaction and degree of cure for the resin. Samples ranging in mass from 20 to 23 mg were placed and sealed in 40 μL aluminum crucibles. The experiment was carried out, utilizing a constant flow of nitrogen at 10 mL/min. The analyses include (1) Isothermal tests at 120 °C, 150 °C and 177 °C to correspond to the cure temperatures, and (2) Dynamic tests at a heating rate of 5 °C /min from -25 °C to 300 °C to calculate the enthalpy of reaction.

3 Results and Discussion

3.1 In-Situ Cure Shrinkage

The analysis of displacement resulting from cure shrinkage is performed on a 5 cm × 5 cm area in the middle of the resin sample, as shown in Fig. 1b. The out-of-plane displacement at the end of the cure cycle spatially varies from -0.414 mm to -0.628 mm, with an average of -0.52 mm. The thermal fluctuations and the resin's convective flow properties as it is heated are responsible for these fluctuations.

The post processing analysis of DIC using VIC-3D software computes the out-of-plane displacement (u_z). The corresponding strain (ε) is calculated using this displacement and the initial thickness (l) as:

$$\varepsilon = \frac{u_z}{l} \tag{1}$$

In Fig. 2 the continuous evolution of strain during the cure cycle for the three curing temperatures is plotted. The error bars represent the standard deviation of the data obtained from the three tests for each isothermal condition. Figure 2a corresponds to the isothermal cure at 120 °C for 180 min. The initial rise in the strain curve during the heating stage is due to the thermal expansion of the resin-binder mix. Average strain of 0.65 is observed during the heating stage. In the isothermal stage the crosslinking of molecules results in an overall shrinkage with the average strain dropping to -0.259. There is a small increase in the strain during the cooling stage attributed to thermal relaxation. An average strain of -0.206 is observed at the end of the cure.

Figure 2b shows similar plot of strain evolution for the 150 °C cure. The average strain of 0.765 is observed during the heating stage, which is higher than that corresponding to the 120 °C cure. During the isothermal stage, the resin shrinkage results in the decrease in strain which varies between -0.20 to -0.30. Again the thermal relaxation increases the strain to a value of -0.118 at the end of the cure cycle. Figure 2c corresponds to a 45 min cure at 177 °C. The strain evolves in a similar manner, however the strain increase due to thermal expansion during heating and the relaxation during cooling are both higher at this temperature.

3.2 Degree of Cure

The cure-kinetics for three cure cycles was characterized using the DSC. The degree of cure was analyzed following the procedure described in [9]. Here, the degree of cure (α) is calculated as:

$$\alpha(t) = \frac{\Delta H_T - \Delta H_R}{\Delta H_T} \tag{2}$$

where, ΔH_T is the total enthalpy of reaction measured in a dynamic scanning test by heating the uncured specimen at a predefined heating rate till the resin is completely polymerized. In the current case, curing of EPON-862 is an exothermic reaction with a ΔH_T of 421.10 J/g.

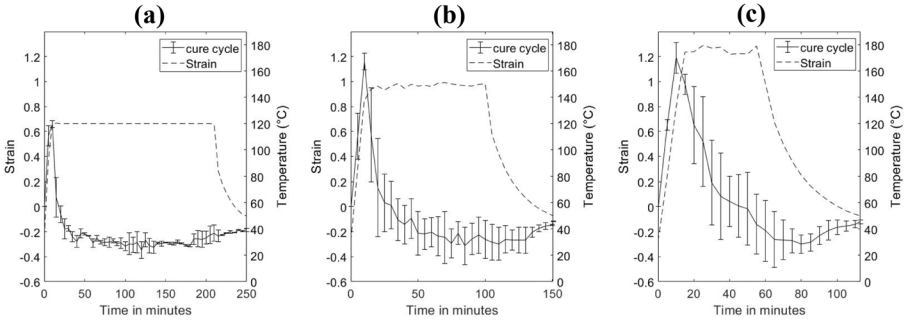

Fig. 2 Strain evolution as function of curing time and temperature for **a** 120 °C cure, **b** 150 °C cure, and **c** 177 °C cure. The error-bars correspond to standard deviation from three tests

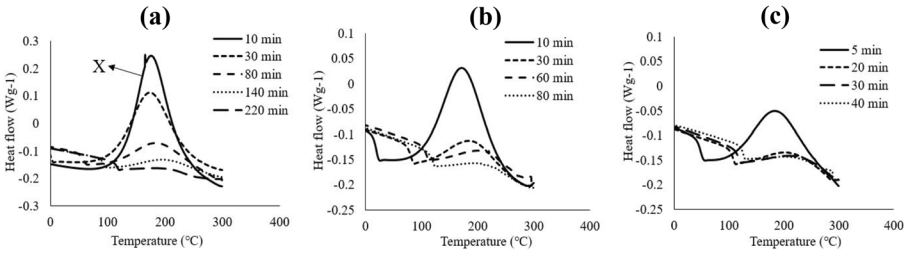

Fig. 3 Heat flow versus temperature at various cure times for isothermal tests at **a** 120 °C, **b** 150 °C and **c** 177 °C

ΔH_R is the residual heat of reaction, i.e. the difference between total enthalpy and the heat of reaction corresponding to isothermal curing for a specified time and temperature. Figure 3 shows the heat-flow (Watts/gm) from the isothermal tests used to calculate the residual heat of reaction. For example, consider the curve X in Fig. 3a. This corresponds to the residual heat of reaction for 10 min at 120 °C. In this case, the total heat of reaction for complete curing (ΔH_T) is split between: (a) enthalpy corresponding to isothermal test at 120 °C for 10 min, followed by (b) ΔH_R from the dynamic scanning test which results in the exothermic peak corresponding to curve X. ΔH_R is obtained as the area under the curve X in Fig. 3a. The cure state for 10 min of cure at 120 °C can then calculated using Eq. (2). This procedure is used to obtain the cure state curves in Fig. 4a. It can be observed from Fig. 3 that the residual heat of reaction decreases with an increase in isothermal cure time, and for higher temperatures. For the 120 °C cure, 98% of the resin is cured after 220 min. Complete cure was obtained after 90 min for 150 °C cure, and 40 min for the 177 °C cure.

3.3 Discussion

Figure 4a, b compare the evolution of the degree of cure, and strain for the 120 °C and 177 °C cures. There are three distinct stages in the curing process with corresponding mechanisms for strain evolution. During ramp-up most of the strain is due to the thermal expansion of monomer resin and binder mix. This corresponds to OA in Fig. 4b for 120 °C and OA' for the 177 °C respectively. Here A and A' correspond to the time at which the

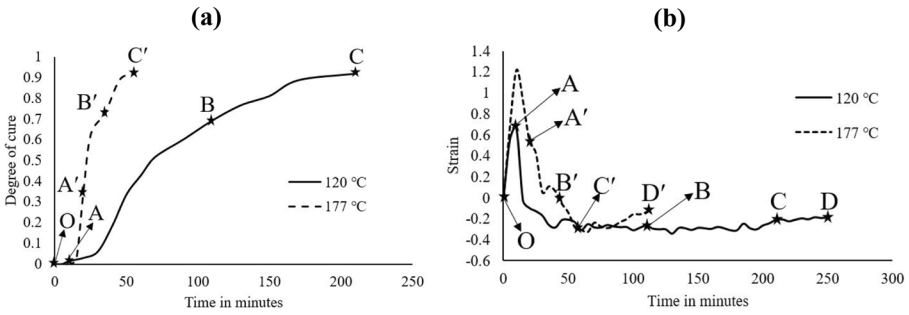

Fig. 4 **a** Degree of cure for EPON 862 cured at 120 °C and 177 °C. **b** Strain for EPON 862 cured at 120 °C and 177 °C

isothermal temperature is reached. The corresponding degree of cure is shown in Fig. 4a. The OA time period for the 120 °C cure is 10 min and the degree of cure at this point is 3%. This suggests that strain of 0.65 at point A is primarily due to the expansion of the monomer EPON-862 and DETDA mix. For the 177 °C the isothermal temperature is reached in 20 min. The polymer has a corresponding degree of cure of 36% by this stage. In this case, the strain is due to two mechanisms, an initial thermal expansion of the monomers combined with the chemical shrinkage due to polymerization. For the corresponding plot in Fig. 4b it can be noticed that the strain shoots to 1.19 within the first ten minutes and then drops to 0.64 in twenty minutes. The initial strain peak is due to thermal expansion and subsequent contraction is due to the cure shrinkage. The 150 °C cure has similar behavior.

The points B and B' correspond to the middle of isothermal stage. For the 120 °C cure, this corresponds to 110 min and the corresponding degree of cure is 76.8%. The compressive strain from point A to B is entirely due to the polymerization shrinkage. Similar contraction due to cure shrinkage is observed for 177 °C cure. The points C and C' correspond to the end of isothermal stage. The degree of cure plots end at these points indicating that the polymer is completely cured (98% and 97% respectively) by this stage. The cure shrinkage is higher in the initial stage of polymerization, i.e. before points B and B'. The change in strain from these points to the end of isothermal stage is relatively low. The strain due to thermal relaxation of the cured epoxy during the cool down is captured in CD and C'D' regions in Fig. 4b. The thermal expansion coefficient for uncured resins are typically higher than that for cured epoxy [10], hence the thermal strains are much higher during ramp-up compared to the cool down.

The behavior of neat resin studied here can be useful in interpreting how the residual stresses and associated defects evolve during composite manufacturing. The overall strains for composite are expected to be lower because the stiffer fibers resist the resin deformations, which leads to residual stresses. Additional factors such as, mismatch of thermal expansion, directionality of fibers, and large difference in elastic moduli come into play. The evolution of residual stresses in composites is determined by the matrix strain evolution as shown in Fig. 4 combined with the aforementioned factors. In a recent study, an experimental approach similar to the current work was used to evaluate defect formation in prepreg composites [11]. In this case, the speckle pattern could be directly applied on the prepreg ply. The movement of the speckle pattern on the top-ply during curing was used to analyze evolution of defects like wrinkles, and also to study processing induced strains and residual stresses [12].

4 Conclusion

A novel approach for in-situ characterization of resin shrinkage is developed using DIC in the composite manufacturing environment. The deformations in the resin are correlated to cure state obtained from DSC. The strain evolution in the epoxy is based on multiple mechanisms. During the initial ramp-up, the thermal expansion of monomer and binder mix leads to a large strain build-up. This is followed by contraction due to the polymerization shrinkage, and a final relaxation of the cured resin. The behavior of neat resin studied in the composite manufacturing environment can be useful in interpreting how residual stresses and associated defects evolve during composite manufacturing.

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Data Availability The data will be made available on request.

Declarations

Conflict of Interest The authors have no conflicts of interests to declare.

References

1. Dusek, K.: Network formation in curing of epoxy resins. Adv. Polym. Sci. **78**, 1–59 (1986). https://doi.org/10.1007/bfb0035356
2. Wisnom, M.R., Gigliotti, M., Ersoy, N., Campbell, M., Potter, K.D.: Mechanisms generating residual stresses and distortion during manufacture of polymer-matrix composite structures. Compos. Part A Appl. Sci. Manuf. **37**, 522–529 (2006). https://doi.org/10.1016/j.compositesa.2005.05.019
3. Snow, A.W., Armistead, J.P.: A simple dilatometer for thermoset cure shrinkage and thermal expansion measurements. J. Appl. Polym. Sci. **52**, 401–411 (1994). https://doi.org/10.1002/app.1994.070520305
4. Shah, D.U., Schubel, P.J.: Evaluation of cure shrinkage measurement techniques for thermosetting resins. Polym. Test. **29**, 629–639 (2010). https://doi.org/10.1016/j.polymertesting.2010.05.001
5. Kravchenko, O.G., Kravchenko, S.G., Casares, A., Pipes, R.B.: Digital image correlation measurement of resin chemical and thermal shrinkage after gelation. J. Mater. Sci. **50**, 5244–5252 (2015). https://doi.org/10.1007/s10853-015-9072-3
6. EPON-862\Epikure W technical data sheet. https://www.miller-stephenson.com/wp-content/uploads/2016/08/W.pdf. Accessed 06 Jan 2021
7. Yoneyama, S., Murasawa, G.: Digital image correlation. Exp. Mech. (2009)
8. Correlated solutions, https://www.correlatedsolutions.com/vibration-fatigue-module. Accessed 06 Jan 2021
9. Hardis, R., Jessop, J.L.P., Peters, F.E., Kessler, M.R.: Cure kinetics characterization and monitoring of an epoxy resin using DSC, Raman spectroscopy, and DEA. Compos. Part A Appl. Sci. Manuf. **49**, 100–108 (2013). https://doi.org/10.1016/j.compositesa.2013.01.021
10. Fu, Y., Michopoulos, J.G., Song, J.H.: On investigating the thermomechanical properties of cross-linked epoxy via molecular dynamics analysis. Nanoscale Microscale Thermophys. Eng. **21**, 8–25 (2017). https://doi.org/10.1080/15567265.2016.1263696
11. Chava, S., Namilae, S.: In situ investigation of the kinematics of ply interfaces during composite manufacturing. J. Manuf. Sci. Eng. Trans. ASME. **143**, 1–10 (2021). https://doi.org/10.1115/1.4047740
12. Chava, S., Namilae, S.: Continuous Evolution of Processing Induced Residual Stresses in Composites: An In-situ Approach. In: Composites: Part A (In Print)