



Chapter 11

Thermo-Mechanical Properties of Thermoset Polymers and Composites Fabricated by Frontal Polymerization

M. Yourdkhani, B. Koohbor, C. Lamuta, L. M. Dean, P. Centellas, D. G. Ivanoff, I. D. Robertson, S. R. White, and N. R. Sottos

Abstract Thermoset polymers are commonly used as the matrix material in fiber-reinforced polymer composites (FRPCs) due to their good mechanical properties, chemical stabilities, and ease of manufacturing. Conventional curing of thermosets and their composites requires heating the matrix monomers at elevated temperatures during long cure cycles for producing fully crosslinked polymers, resulting in high manufacturing cost in terms of time, energy, and capital investment. Frontal polymerization (FP) is a promising approach for rapid, energy-efficient fabrication of high-performance thermosets and FRPCs. In FP, a thermal stimulus (trigger) causes a self-propagating exothermic reaction wave that transforms liquid monomers to fully cured polymers, eliminating the need for external energy input by large ovens or autoclaves. We have used the FP of dicyclopentadiene (DCPD) to successfully fabricate thermoset polymers and composite parts. In this novel curing strategy, the final degree-of-cure of the polymer, and thereby its mechanical performance, is governed by the heat transfer phenomenon that occur at the polymerization front. During the fabrication of FRPCs some fraction of the generated heat is absorbed by continuous fibers or lost through the tooling. In this work, we will discuss the characterization of the thermo-mechanical properties of DCPD polymer manufactured by FP curing.

Keywords Frontal polymerization · Polymer composites · Digital image correlation · Residual stress · Advanced manufacturing

Thermoset polymers are generated via the formation of irreversible 3D crosslinking networks between monomers often facilitated by applying external energy in the form of heat or light. The resulting crosslinked network yields the polymer thermally stable with superior mechanical performance and high glass transition temperature (T_g) compared to thermoplastic counterparts. As a result, thermosets have been widely used in high-performance, light-weighting applications in aerospace, automotive, marine, and energy industries. In particular, the matrix polymer in fiber-reinforced polymer composites is typically composed of a thermoset such as epoxy. Current technologies for the manufacturing of high-performance polymeric and composite parts rely on curing in large autoclaves or ovens, leading to high manufacturing time, energy, and cost. It is highly desirable to cure these polymers with less energy to reduce their cost and carbon footprint and further their applications.

M. Yourdkhani (✉) · C. Lamuta

Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, IL, USA
e-mail: yourd@illinois.edu

B. Koohbor · L. M. Dean · D. G. Ivanoff · N. R. Sottos

Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, IL, USA
Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, USA

P. Centellas · S. R. White

Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, IL, USA
Department of Aerospace Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, USA

I. D. Robertson

Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, IL, USA
Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA

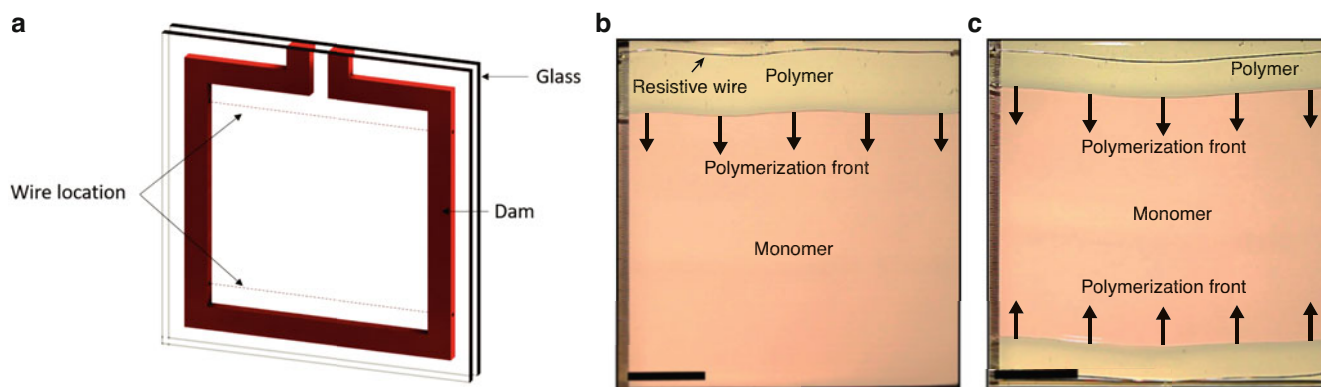


Fig. 11.1 Triggering modes of frontal polymerization. (a) Schematic of the open glass mold used to manufacture polymer panels. (b) One resistive wire embedded in the mold and connected to a power source initiates the reaction that propagates from top to bottom. (c) Two resistive wires on the opposite ends of the molds trigger the reaction simultaneously, where the reaction fronts propagate in opposite directions and merge at the middle of the mold. The scale bar is 2.5 cm

One promising approach to substantially reduce the manufacturing time and energy is to employ the enthalpy of polymerization to produce the necessary thermal energy for curing the polymer rather than using external energy. Frontal polymerization (FP) is a propagating reaction wave based on the heat release of an exothermic polymerization reaction [1]. A solution of monomer and latent initiator is heated locally until the initiator is activated, producing heat from polymerization, and further accelerating the reaction. The result is a propagating wave of polymerization, which rapidly polymerizes the available monomers. The manufacturing time of a product is thereby directly dependent on the front speed as well as the traveling distance of the front. Using more than one thermal trigger point at different locations allows for reducing the travel distance, and consequently, the manufacturing time, which is of great importance in manufacturing of large components.

Here, we have used the FP of dicyclopentadiene (DCPD) [2] to produce high-performance thermoset and FRPC parts. The FP reaction is initiated by applying an electrical current through a resistive wire embedded in an open glass mold (Fig. 11.1a, b) or composite layup for manufacturing neat resin and FRPC panels, respectively. The frontal speed in the neat resin and FRPC is 7.5 and 10 cm/min, respectively. Using two resistive wires in opposite ends of the glass mold (Fig. 11.1c) or composite layup reduces the manufacturing time by half compared to a single triggering mode. However, as the two fronts merge, the heat produced by the monomers in opposite fronts cannot be removed and will lead to the formation of a thermal spike that may result in undesirable volume changes, variation in material properties, or creation of residual stresses. The present study aims at understating the effect of the thermal overshoot that occurs during the merging of two fronts on the mechanical properties of produced polymer parts.

Local mechanical response of neat polymer samples is evaluated through full-field strain measurements facilitated by Digital Image Correlation (DIC). DIC area of interest is selected such that merged front area would remain within the field of view throughout the entire experiment. Time-lapse images are acquired from the speckled area of interest at a rate of 1 Hz, synchronized with load-cell data sampling rate. Images are post-processed in the DIC software Vic-2D to obtain the full-field distribution of in-plane strain components. Figure 11.2 shows representative contour maps obtained at different global stress levels. Strain localization is evident at near-to-failure stress levels for double front polymerized samples. Possible mechanisms giving rise to such localized strain response will be discussed in the presentation.

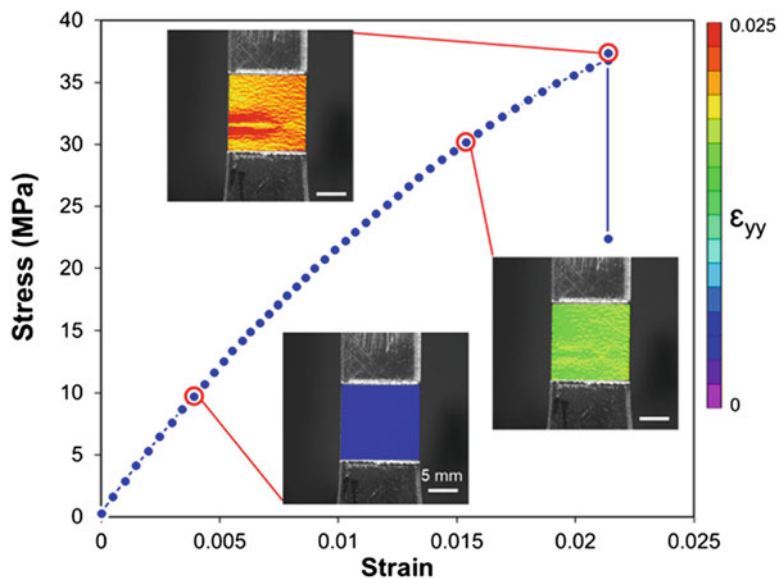


Fig. 11.2 Contour maps showing the distribution of vertical in-plane strain component, ϵ_{yy} , at various stress levels. Tensile load is applied in y -direction

Acknowledgement This work was supported by the United States Air Force Office of Scientific Research through award FA9550-16-1-0017.

References

1. Pojman, J.A.: Frontal Polymerization. In: Matyjaszewski, K., Möller, M. (eds.) *Polymer Science: A Comprehensive Reference*, pp. 957–980. Elsevier (2012)
2. Robertson, I.D., et al.: Alkyl phosphite inhibitors for frontal ring-opening metathesis polymerization greatly increase pot life. *ACS Macro Lett.* **6**(6), 609–612 (2017)