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Catalyzed frontal polymerization-aided 3D printing of epoxy thermosets

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ABSTRACT

Frontal polymerization is a self-propagating exothermic reaction and provides a rapid and energy-efficient way to manufacture thermosets. A critical issue for frontal polymerization is to concurrently maintain a low frontal temperature and a self-sustained frontal propagation, which significantly depends on the frontal velocity. In this work, carbon nanotubes (CNTs), graphene oxide(GO) and discontinuous carbon fibers (d-CFs) were incorporated into epoxy thermosets to tune the frontal polymerization. Their catalytic effects on frontal temperature and frontal velocity were studied. Both CNTs and GO were found to significantly reduce the activation energy of frontal polymerization, whereas d-CFs did not show any obvious effect on the activation energy. The real-time non-destructive characterization showed that 1wt % CNTs incorporation reduced the frontal temperature from 240 to 227°C while the front velocity remained the same (6.5 cm min^{-1}), indicating effective decoupling frontal temperature from frontal velocity. The frontal temperature could be further reduced to 220°C or lower at an increasing loading of CNTs while the frontal velocity remained the same. In contrast, 1wt% GO incorporation reduced the frontal temperature from 240 to 220°C, but also decreased the frontal velocity from 6.5 to 5.1 cm min^{-1} (21.5% reduction). In addition, as-prepared CNTs-incorporated epoxy resins were used in the 3D printing process via frontal polymerization and their printability were demonstrated. This discovery opens a new pathway for additive manufacturing through catalyzed in-situ frontal polymerization.

1. Introduction

Polymer composites have been extensively used in versatile industries due to their high strength-to-weight and easy manufacturing. Among polymer composites, thermosets have received much attention from scientists and industries since last century because of their excellent mechanical property, chemical resistance, and low-cost features. Conventional manufacturing of thermosets and their composites requires hours of autoclave processing at elevated temperatures to create crosslinked polymer networks [1–3]. It is not only energy-intensive and time-consuming, but also detrimental to the environment due to massive carbon emission during conventional manufacturing [4,5]. Moreover, it was difficult for conventional manufacturing to fabricate parts with complex geometry, and thus hard to achieve customized design and production.

Additive manufacturing (AM), alternatively called 3D printing, is a technology that fabricates a part using computer-aided design (CAD) to deposit materials layer by layer and has been considered as the next-generation manufacturing approach. In-situ curing, especially frontal curing, is a promising method for thermosets fabrication because of high energy-efficiency and significant time-saving. Frontal polymerization discovered by Chechilo et al in early 1970s, is a process that starts with an initial thermal stimulus and then self-propagates in an exothermic reaction wave [6–8]. It has shown a great potential for in-situ curing of thermosets. Although the frontal polymerization-based in-situ curing has been demonstrated in some thermosets including dicyclopentadiene (DCPD), epoxy resin, and vinyl- epoxy resin mixtures [9–12]. Epoxy resins demonstrated low frontal curing velocity [5,13], and thus frontal propagation is difficult to be sustained. As a result, early termination of the front propagation always happened [14–19]. Therefore, a self-sustained frontal polymerization is required to ensure the in-situ curing synchronized with the printing process.

The addition of catalysts provides an effective way to compensate for the low reactivity of the matrix materials and has been reported for traditional molding processing of thermosetting materials [20,21]. Carbon-based materials, such as carbon nanotubes (CNTs) and graphene oxide (GO) are regarded as effective catalysts which can generate new transition intermediates to facilitate the chemical reaction [22–24] . It was reported that CNTs can serve as a catalyst to decrease the curing reaction temperature, lower the activation energy, and to accelerate the initial curing reaction of the epoxy resin [25,26]. Although some ef-

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forts have been made to explore the carbon-based nanocatalyst for the conventional manufacturing of thermosets, no attempt has been made to study their catalytic effects in frontal polymerization toward in-situ curing synchronized 3D printing.

In this work, one-dimensional (1D) and two-dimensional (2D) carbon-based materials were added to the bisphenol A diglycidyl ether (BADGE) epoxy resin. Their catalytic effects on the activation energy, front velocity and temperature of frontal polymerization were studied. The resultant mixtures were also applied to the 3D printing process that was synchronized with the frontal polymerization-induced in-situ curing.

2. Experimental

2.1. Materials

Epoxy resin (EPON 828) containing bisphenol A/epichlorohydrin was purchased from Hexion. Thermal initiator 1,1,2,2-tetraphenyl-1,2-ethandiol (TPED, noted as I-TI) was purchased from Sigma Aldrich. Cationic initiator, bis[4-(tert-butyl)phenyl]iodonium Tetra(nonafluoro-tert-butoxy)aluminate (noted as: I-Al) was purchased from TCI America. Multiwall carbon nanotube (Multiwall CNT) was purchased from Sigma Aldrich. Flake graphite powder (Grade 230) was kindly provided by Asbury Carbons.

2.2. Ink preparation

For composite inks, different fillers including CNTs, GO, and discontinuous carbon fibers(d-CFs) were mixed with epoxy resin before the addition of I-Al and I-TI in the mixture. CNT/epoxy composites inks were prepared with CNT concentrations ranging from 0.2wt% to 1wt% in this study. CNTs and d-CF fillers were used as received. GO was prepared using the modified Hummer's method [27]. The morphology and dimension of the GO were similar to those reported in our previous literatures [27]. I-Al and I-TI were dissolved in solvents (Dichloromethane, DCM) and then mixed with epoxy resins to produce the reactive neat resins. Solvent was subsequently removed through rotary evaporation after stirring for hours.

2.3. Frontal polymerization aided printing

Carbon fillers/epoxy resin mixtures were loaded into the syringe and dispensed out of the nozzle to replicate 3D structures defined by the computer model. Allevi 1 3D bioprinter was used for the printing demonstration. A flexible heater (New Era, 33W, 2 thermocouple, 90cm cord, 1.5cm
×50cm flat to spiral heating pad) was applied onto the platform for initiation. The thermocouple was set to 120°C for initiation. The syringe was fixed in the printhead and kept at room temperature during printing. The curing started in a few seconds after the mixture was deposited onto the heated platform and then heat propagated along the print path to solidify as-deposited 3D structures.

2.4. Rheology measurements

Rheological behavior was characterized via a rheometer (TA Instruments AR-G2) equipped with a 10-mm diameter parallel plate. Mixtures of epoxy resin with different initiator concentrations and filler concentrations were used for the measurement. The viscosity was measured against the different shear rates.

2.5. Thermal analysis

Differential scanning calorimeter (DSC) (Q20, TA Instruments) equipped with a CFL-50 cooling system was used for the thermal analysis. Epoxy-resin based mixtures in a range of 2-5mg were added into aluminum hermetic DSC pans and sealed. A large amount of mixture may cause thrust temperature variation because of the highly exothermic nature of the resin. The reaction enthalpy was calculated by the total area of heat flow after baseline correction. The isothermal heat flow was used for activation energy calculation.

2.6. Activation energy calculation

Isothermal tests at three different curing temperatures were carried out for different formulations of the mixtures. The resultant heat flow vs. curing temperature and heat flow vs. curing time were used to calculate the reaction rate and conversion rate at each time interval. A second order reaction model was used for fitting the curing reaction to obtain the curing kinetics parameters, as shown in Equation 1.

$$\frac{\partial \alpha}{\partial t} = \left(k_1 + k_2 \alpha^m\right)(1 - \alpha)^n \tag{1}$$

Where α represents the degree of curing; $\frac{d\alpha}{dt}$ indicates the rate of reaction which can be obtained by calculating the change of α at a time interval; k_1, k_2, n, m are curing kinetics parameters. The curing kinetics parameters obtained at different isothermal curing temperatures were then linearly fitted to estimate activation energy.

2.7. Front velocity and front temperature analysis

The infrared (IR) camera (FLIR A325sc) recorded the temperature profile as printing continued, and the resultant IR images were processed to obtain frontal velocity and frontal temperature. The measurement was conducted three times for each data point shown in this study.

3. Results and discussion

3.1. The Effect of Carbon Fillers on the Activation Energy

The heat flows at different reaction temperatures were characterized by DSC, as shown in Fig. 1(a). 1wt% CNTs-incorporated resin showed a peak reaction rate at a lower temperature (121°C), indicating an effective catalytic effect. The incorporation of 1wt% GO into resin reduced the peak reaction temperature down to 106 °C, indicating a more effective catalytic effect. The lower peak reaction temperature may result from the entrapment of epoxy monomers or oligomers, reducing a greater amount of the free molecular segments [25]. In contrast, the incorporation of microscale d-CF did not show any obvious catalytic effect on the peak reaction temperature. This might be contributed to the significant steric hindrance effect on the epoxy curing pathway. The lowered peak temperature might imply catalytic curing reaction and thus the activation energy was calculated for each specific resin formulation to quantitatively understand the effects of CNTs, GO and d-CF on the curing kinetics of the epoxy resin system, respectively. The activation energy was derived by fitting the isothermal curing profiles to the cure kinetics model. The calculated activation energies for the reaction systems incorporated with different fillers (1wt% CNT, GO, and d-CF, respectively) are shown in Fig. 1(b). The incorporation of CNTs and GO reduced the activation energy in the curing reaction, which was consistent with the decreasing peak temperature shown in Fig. 1(a). The reduction of activation energy might be caused by the formation of new transition states for the epoxide-ring opening reaction. Specifically, the nucleophiles that originated from the I-Al might approach the defect sites or the end of CNT [28] to form the new nucleophiles with lower energy barriers to attack the carbon-oxygen bonds in the epoxide group. However, the incorporation of d-CFs may not lead to a similar effect due to their large size and potential steric hindrance effect.

3.2. The effect of fillers on frontal curing reaction

Since CNTs and GO significantly reduced the curing activation energy, it is believed that they can catalyze the frontal curing behav-

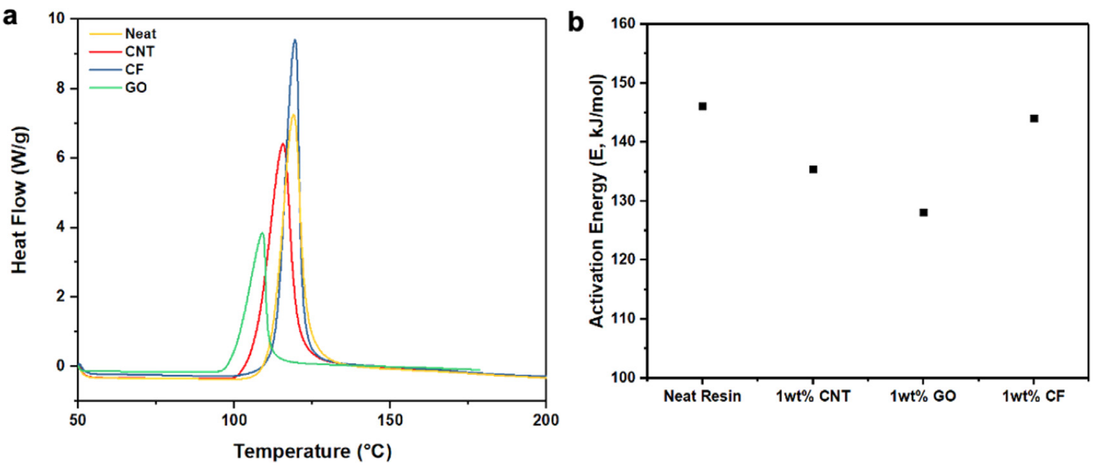

Fig. 1. (a) DSC curves of neat resin and carbon filler/epoxy resins. (b) The activation energy of curing reactions of neat resin and carbon filler/epoxy resins.

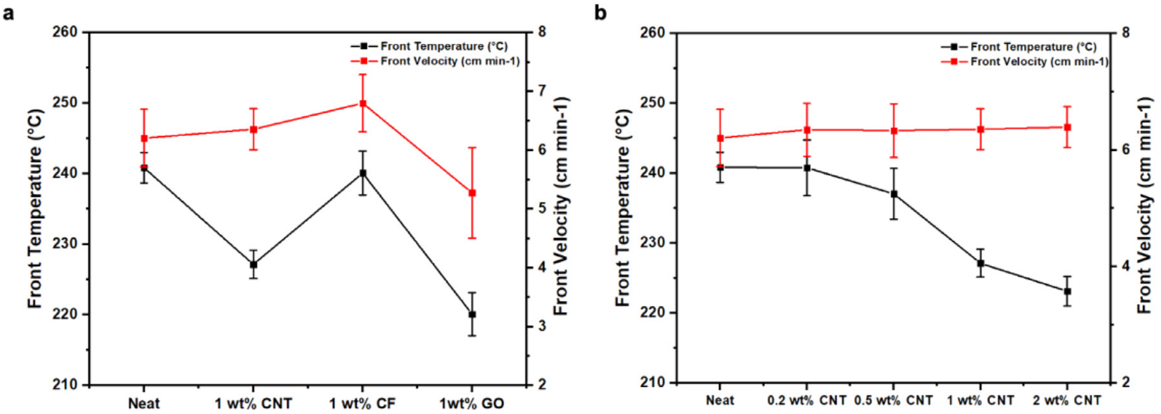

Fig. 2. (a) Comparison of the front temperature and front velocity among neat resin and carbon fillers/epoxy resins. (b) The effect of CNTs concentration on the front temperature and front velocity of CNTs-filled epoxy resins.

iors. CNTs, GO and d-CFs were incorporated into the epoxy resins, respectively. Their frontal propagation behaviors were studied and analyzed via non-destructive IR imaging analysis. The results are shown in Fig. 2(a). Briefly, the IR camera was positioned towards the specimen at a certain angle and captured a series of IR heatmaps. V_f was obtained by taking these heatmaps at certain time stamps and examining their positions of these boundaries to the origin, and the velocity at each timestamp was calculated by the distance difference between the boundaries of two consecutive heatmaps divided by the elapsed time. T_f was recorded as the temperature at these boundaries. Fig. 2(a) shows that CNTs could reduce T_f while maintaining V_f compared to the neat resin. This phenomenon is different from what was observed in the neat resin. The adjustment of initiator concentrations in the neat resin results in the simultaneous increment or reduction of T_f and V_f as shown in the previous study [29]. Combined with the previous DSC analysis, CNTs altered the reaction curing kinetics and reduced the activation energy, and thus changed the front propagation behavior of the frontal reaction, indicating significant catalytic effect in the frontal curing process. The lowered T_f in comparison to the neat resin with the same initiator concentration indicates a more effective heat transfer in the reaction propagation direction. The lowered reaction temperature was consistent with the left shift peak temperature in the DSC results in Fig. 2(a). Compared to CNTs, GO was more effective in reducing T_f ($\sim$220°C), but also lowered V_f, indicating less effective in decoupling frontal temperature and frontal velocity. The difference in the catalytic frontal behaviors of CNTs and GO on the epoxy resins may be caused by the difference in thermal conductivity and the morphology of nanostructure. In contrast, the resins with the inclusion of d-CF showed a higher V_f and T_f, corresponding to a retarded curing reaction.

Among these three types of carbon fillers, CNTs were more effective in reducing temperature while maintaining a high V_f, and thus the effect of CNT filler concentration on V_f and T_f was further studied. The corresponding results are shown in Fig. 2(b). At a higher CNT concentration above 0.2wt%, T_f started to decrease while V_f remained the same. The reduction of T_f was attributed to the altered reaction route and more effective heat dissipation, which further resulted in the reduction of V_f given that higher temperature increased the reaction rate. During the further increment of the CNTs concentration, T_f continued to decrease while V_f remained the same. Specifically, the inclusion of 2wt% CNTs in the epoxy resin can reduce T_f to $\sim$220°C while keeping a similar high V_f. The further increment of CNTs fractions become difficult due to the dispersion challenges.

3.3. *Catalyzed frontal polymerization-aided printing*

The rheological behaviors of the neat epoxy resins with three different curing agent ratios, CNTs/epoxy resins, GO/epoxy resin, and d-CF/epoxy resin were characterized, as shown in Fig. 3(a). When CNT fractions were below 0.5wt%, no noticeable shear thinning behavior was observed. When CNT fractions were above 1wt% fraction, obvious shear thinning behavior was observed. To print epoxy resins with the aid of frontal polymerization, the frontal polymerization velocity should be synchronized with the nozzle deposition speed to ensure decent replication of the computer model. The addition of CNTs could help to lower

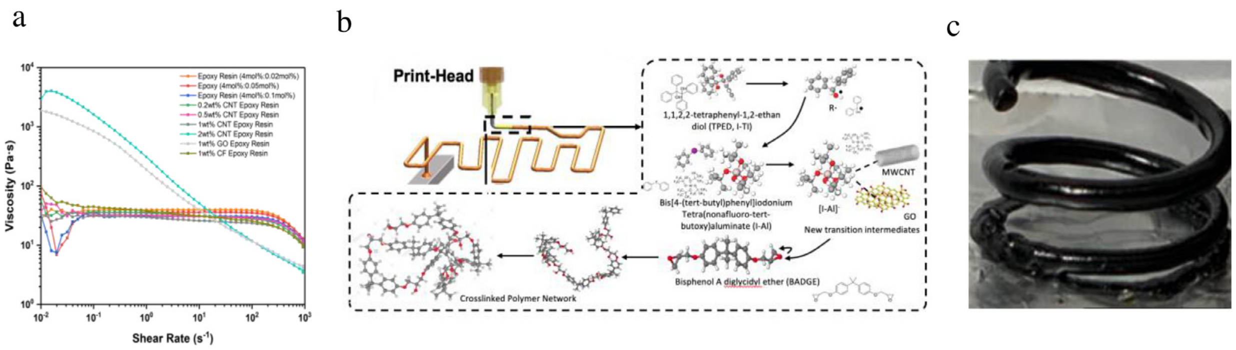

Fig. 3. (a) The rheological results of epoxy resins and carbon fillers/epoxy resins, (b) The schematic diagram of catalyzed frontal curing aided printing, and (c) free-standing spiral structure printed by CNTs/epoxy resins.

the frontal temperature and keep high frontal velocity, and thus facilitate the printability. The catalytic mechanism was illustrated in the Fig. 3(b). In this work, TPED (I-TI) with thermal-thermal labile bond was selected as thermal initiator and I-Al was selected as the cationic initiator. The mechanism was based on radical induced cationic frontal polymerization (RICFP), where the initial heat supply could break the carbon-carbon bond in I-TI. CNTs could donate electrons to molecules when encountering the reaction sites, accelerating the curing reaction. On the other hand, exceptional thermal conductivity could help to facilitate heat transfer and avoid local heat build-up. CNTs/epoxy resin mixture was loaded into the syringe of the Allevi printer, and then extruded to print a spiral structure, which required a good synchronization between in-situ curing and nozzle deposition process. A short movie capturing the printing process was also provided in the supplemental material, confirming excellent printability for the CNTs-filled epoxy resins. However, 1wt% CNTs-filled resins were not printable after storing 4°C for 3 months, indicating a short pot-life of the epoxy resin after CNTs additions.

4. Conclusion

In this work, nano- and micro-carbon fillers including CNTs, GO and d-CF were incorporated in the epoxy resin for printing and in-situ curing. CNTs demonstrated effective decoupling of frontal velocity and frontal temperature. The frontal temperature was reduced from 240°C to 227°C with the incorporation of 1wt% CNT in the resin while the front velocity remained the same. The relatively lower front temperature could effectively avoid local overheating and prevent any degradation during the frontal curing process. In contrast, GO could not effectively decouple the frontal velocity and frontal temperature since GO reduced fontal temperature and frontal velocity concurrently. The d-CF incorporation led to both high frontal temperature and high frontal velocity. The catalytic effects of carbon fillers were dependent on their structures and interactions with the reactant molecules. This study pointed out potential methods in tuning materials toward rapid and energy-efficient freeform fabrication.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.addlet.2022.100030.

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