

Mechanical Characterization of Epoxy Resin Manufactured Using Frontal Polymerization

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ABSTRACT

Frontal polymerization (FP) is a promising alternative manufacturing method for thermoset-based fiber-reinforced polymer composites (FRP) in comparison with the traditional autoclave/oven-curing method, due to its rapid curing process, low energy consumption, and low cost. Optimizing the weight contents of initiators relative to the resin's mass is needed to adjust the mechanical properties of FRPs in industrial applications. This study investigates the effect of varying the photo-initiator (PI) weight content on tensile properties and the frontal polymerization characteristics, including the front velocity, front temperature, and degree of cure, in the FP process of the epoxy resin. Specifically, a dual-initiator system, including PI and thermal-initiator (TI), is used to initiate the polymerization process by ultraviolet (UV) light. The weight content of the TI is fixed at 1 w%, and the relative PI concentration is varied from 0.2 w% to 0.5 wt%. Results show that increasing the PI amount from 0.2 wt% to 0.3 wt% significantly improves the front velocity and the degree of cure by about two times. Increasing the PI content from 0.3 wt% to 0.4 wt% results in 15% and 26% higher degree of cure and front velocity, respectively. Moreover, due to the different front velocity in the top and bottom regions of the specimen, the specimens with 0.4 wt% PI exhibited a curved shape. The specimen with 0.5 wt% PI is thermally degraded and foamed. By comparing tensile properties, it is found that increasing the PI concentration from 0.2 wt% to 0.3 wt% improves the tensile strength and Young's modulus by 3.91% and 7%, respectively, while the tensile strength and the Young's modulus of frontal polymerized specimens are on average 8% and 14% higher than traditionally oven-cured ones, respectively.

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INTRODUCTION

Nowadays, the growing demand for sustainable and additive manufacturing processes for thermoset-based fiber-reinforced polymer (FRP) composites continuously to drive emerging out-of-oven/autoclave manufacturing techniques. Traditional manufacturing and repair of FRP composites require prolonged curing duration and intensive energy consumption for cross-linking and consolidation, which are typically achieved through the thermal curing method using an oven or an autoclave. When compared to this traditional method, frontal polymerization (FP) provides a promising alternative due to the rapid curing, reduction in energy consumption that impacts the environment, and the ease of manufacturing [1-3]. FP generates a self-propagating exothermic reaction zone, *i.e.*, a curing front, using an initial localized triggering mechanism, *e.g.*, a thermal or UV-induced external source, which converts the cold beyond monomer region to a hot-formed polymer. The frontal polymerization characteristics, including the front velocity, degree of cure, and polymer degradation, are highly affected by the weight contents of the photo-initiator and the thermal-initiator in relative to the monomer [2, 4].

Due to their robust reactivities and low exothermicities, the acrylate resin systems, which are extensively studied, naturally lend themselves to FP in contrast to epoxide resin systems. Mariani *et al.* [5] investigated the FP characteristics of poly(dicyclopentadiene) (pDCPD) via the frontal ring opening metathesis polymerization (FROMP) process. Robertson *et al.* [6] studied the effect of different fiber volume fractions of carbon FRPs on FP characteristics and tensile strength compared to those fabricated through the thermal curing method. They showed that the frontal polymerized specimens had comparable tensile and flexural strengths with those of the traditionally oven-cured specimens. In another study, Centellas *et al.* [7] demonstrated the effects of different boundary conditions and multiple-triggering directions on FP characteristics. They indicated that insulated boundary conditions and using two triggering points instead of one can reduce the curing duration, when compared to using a single triggering point. Although many studies have demonstrated the success of FRPs with DCPD resin, their use in additive manufacturing and the industrial application of this material system are limited due to its short pot life of a few hours [8].

In contrast, epoxy-based monomers are extensively utilized in the fabrication of FRPs in the industry [9, 10]. This type of monomer can be polymerized using the FP technique, more specifically, the radical-induced cationic frontal polymerization (RICFP) technique [11]. This method provides a longer resin pot life along with more practical applications in industry, in contrast with acrylate-based resins, such as DCPD. This is enabled due to the ability to use two separate initiator systems in RICFP of epoxide systems. This configuration stabilizes the resin mixture so that it remains intact for a month at a 50 °C dark-ambient temperature [12]. For instance, Tran *et al.* [13] characterized the FP process and mechanical properties of carbon fiber reinforced polymer (CFRP) composites using bisphenol A diglycidyl ether (BADGE), diaryliodonium tetrakis (perfluoro-*tert*-butoxy) aluminate, and benzopinacol as monomer, photo-initiator and thermal initiator, respectively. The fiber volume fraction was 35%, and the mechanical properties were found to be similar to those manufactured using the traditional thermal curing method. In another study, 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate

(ECC) monomer, which has a similar molecular structure to industrial resin, and sulfonium salts were employed for photo-curing of CFRP with 40% of the fiber volume fraction [14]. They reported that the dual initiation system can increase the front velocity up to 13 cm/min, when compared to using a single initiation system with a reported front velocity of 5.3 cm/min [13].

As mentioned before, the weight contents of PI and TI in relative to the monomer resin is critical in the FP process, which controls the front temperature and the heat generation, and hence, the degree of cure and the frontal velocity. Although existing studies have shown the frontal polymerization process of neat resin and FRP cases corresponding to the different epoxide systems with various single- or dual-initiator systems, the effects of initiator concentrations on the FP process and the resulting mechanical properties still need to be investigated. Thus, this study investigates the FP performance of epoxy resin. Standard tensile specimens (*i.e.*, ASTM D638-14 [15]) were fabricated using the UV-induced FP process with varying weight contents of the PI. The tensile properties, FP characteristics, including the temperature, front velocity, and degree of cure, were characterized. Moreover, the tensile properties of frontal polymerized specimens are also compared with properties of those fabricated via the traditionally oven curing method.

METHODOLOGY AND EXPERIMENTAL TESTS

Materials

(3,4-epoxycyclohexane)-methyl-3,4-epoxycyclohexyl carboxylate (ECC, AAblocks, Inc.), p-(octyloxyphenyl)phenyl iodonium hexafluorostibate (IOC-8 SbF₆), and benzopinacol are mixed as epoxy monomer, photo-initiator (PI), and thermal-initiator (TI). Also, isopropylthioxanthone is used as a photosensitizer (PS). This material system is employed for RICFP specimens. In order to produce oven-cured specimens, the monomer is thermally cured with cycloaliphatic 4-methylhexahydrophthalic anhydride (MHHPA) and Tertiary amine N,N-dimethylbenzylamine (DMBA) as the curing agent and catalyst, respectively. The material used for the mold of the epoxy resin specimens is silicone elastomer. The frontal polymerization is initiated utilizing a mercury arc lamp UV source (500 W with a spot size of 1 cm in diameter).

Sample Preparation

The initiators and photosensitizer are dissolved in the epoxy monomer using a magnetic stirrer at a high shear rate. Then, the mixture was poured into the silicone elastomer mold and degassed under high vacuum pressure for 18 hours at room temperature before conducting the frontal polymerization. Based on [15], the mass ratios of the TI and the photosensitizer were fixed at 1 wt% and 0.05 wt% relative to the mass of the epoxy monomer, respectively. The mass ratio corresponding to the PI was varied between 0.1 wt% and 0.5 wt%. It is noted that three grams of epoxy monomer was used for each sample. For each specific mass ratio, three replicate samples were fabricated. The sample identifications are described in Table

I. For fabrication of traditional oven-curing specimens, the epoxy monomer was stirred with curing agent and catalyst for 20 minutes at room temperature, as indicated in [16, 17]. Then, the liquid was cured at 80 °C for 15 hours in the oven. The mass ratio between the MHHPA and ECC is 1.267:1. The catalyst DMBA was mixed with the resin and MHHPA at a 0.0164:1 mass ratio [16, 17].

TABLE I. SAMPLE IDENTIFICATION CORRESPONDING TO THE RICFP SPECIMENS.

No.	Weight contents		
	Thermal-initiator (TI) (wt%)	Photo-initiator (PI) (wt%)	Photo-sensitizer (PS) (wt%)
1	1	0.2	0.05
2	1	0.3	0.05
3	1	0.4	0.05
4	1	0.5	0.05

Experimental Test

The temperature at distinct locations and at the curing front were measured utilizing a FLIR One Pro thermal camera during the frontal polymerization process. Although the polymerization was visible through the thermal camera, it is crucial to also look into the mechanical characteristics of the cured specimens in order to determine whether the frontal polymerization process may be employed as a replacement for traditional autoclave or oven curing procedures. To investigate the effect of the relative ratio of weight contents of PI and TI on the tensile strength and Young's modulus of neat resin specimens, ASTM D638-14 standard tensile tests were conducted [15]. A silicone elastomer mold with a rectangular cavity was used to produce a beam specimen with the same length, thickness, and major width as the type V standard specimen (Fig. 1 (a)). After that, the type V dog-bone specimen, as shown in Fig. 1 (b), is cut out of the beam specimen using waterjet cutting. This procedure is followed for both the traditional oven curing and RICFP specimens.

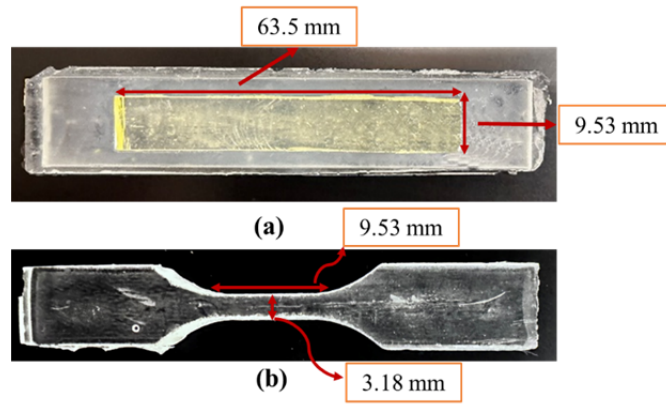


Figure 1. Geometrical representation of (a) beam specimen in the silicone mold and (b) type V standard tensile specimen fabricated after trimming the beam specimen using waterjet cutting.

Furthermore, the degree of conversion is evaluated using Fourier-transform infrared spectroscopy (FTIR) at the top, bottom, and cross-section of the middle part in each specimen. The signals are recorded in a range of $400\text{--}4000\text{ cm}^{-1}$ at 2 cm^{-1} rate over 64 scans. Then, the absorbance peak height ratios of oxirane (789 cm^{-1}) and C=O bond (1724 cm^{-1}) are calculated, which are related to the polymerized (*i.e.*, oven-cured and RICFP) specimens and uncured monomer. The below equation is used to calculate the degree of cure [18]:

$$\text{Degree of cure} = 1 - \frac{\left(\frac{H_{789}}{H_{1724}}\right)_P}{\left(\frac{H_{789}}{H_{1724}}\right)_M}, \quad (1)$$

where H indicates the value of absorbance and subscripts P and M represent the polymer and monomer, respectively.

RESULTS AND DISCUSSION

Recall that this study aims to investigate the effect of the PI weight fraction on the frontal polymerization characteristics and tensile properties of epoxy specimens manufactured by FP in comparison with the oven-cured traditional specimens. The weight contents related to thermal initiator (TI) and photosensitizer (PS) were fixed at 1 wt% and 0.05 wt%, respectively. The frontal polymerization characteristics, including the average front velocity (measured at three points), the initiation time, the total time, and the degree of cure, are shown in Table II.

The temperature was recorded at three different fixed locations at various times, as shown in Fig. 2. The maximum temperature was also recorded, which corresponds to the curing front temperature during the polymerization process. Figure 2 illustrates the temperature history of the RICFP of a neat resin beam specimen with 0.3 wt% PI using a thermal camera. Additionally, the average front velocity is calculated at three different points, *i.e.*, $x = 21.00\text{ mm}$, $x = 31.75\text{ mm}$, and $x = 63.50\text{ mm}$. From Fig. 2,

TABLE II COMPARATIVE PARAMETERS OF FRONTAL POLYMERIZATION CHARACTERISTICS.

Specimen No.	Front velocity (mm/s)		Initiation time (s)	Total time (s)	Degree of cure (%)
1 (PI=0.2 wt%)	x=21.12	1.35	12	107	40
	x=31.75	0.83			
	x=63.5	0.63			
2 (PI=0.3 wt%)	x=21.12	2.82	9.5	57	81.9
	x=31.75	1.67			
	x=63.5	1.08			
3 (PI=0.4 wt%)	x=21.12	4.7	3.5	40	93.47
	x=31.75	2.28			
	x=63.5	1.61			
4 (PI=0.5 wt%)	x=21.12	5.27	2	31	Polymer degraded and foamed
	x=31.75	2.87			
	x=63.5	2.04			

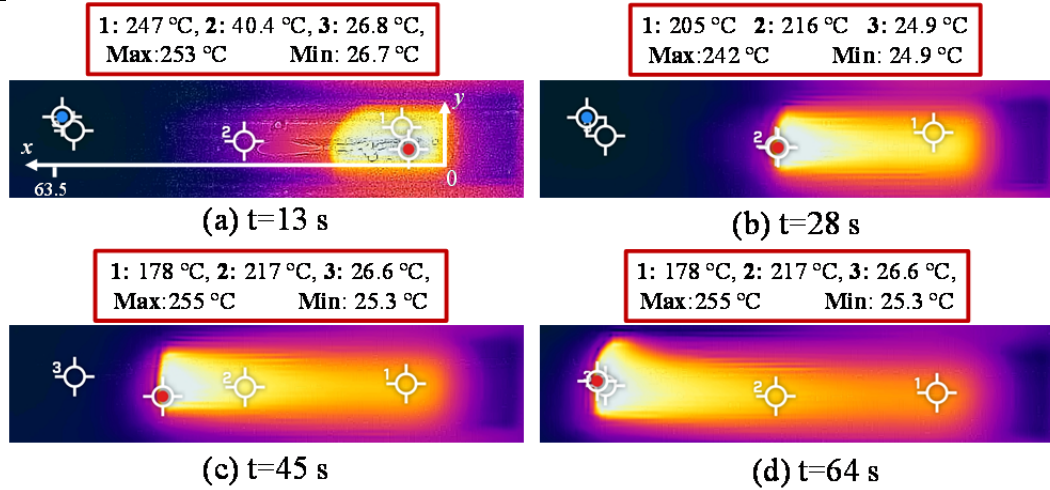


Figure 2. Temperature history recorded from the top surface corresponds to 0.3 wt% PI weight content (*i.e.*, No. 2 specimen).

it can be seen that the front propagated uniformly through the longer dimension of the specimen. Comparing the maximum temperature with the front temperature at $t = 13$ s showed that the location of the initial maximum temperature remains unchanged. This phenomenon is caused by exposing the UV light at one fixed spot, which causes a concentration of exothermic heat at this location. After the curing front propagated through the middle of the specimen, the maximum temperature decreased to about 240 °C, followed by a uniform temperature distribution (Fig. 2(b)). As the curing front reached the end part of the specimen (*i.e.*, the end part of the mold), the maximum temperature started to increase to 250 °C. This can be explained by the increased generation of exothermic heat concentration due to the insulating boundary condition. Specifically, due to the low thermal conductivity of the silicone elastomer mold, the generated exothermic heat is trapped in the end part of the mold, which resulted in the aggregation of heat and an increase in the temperature. This behavior was observed for all specimens containing different amounts of PI.

By comparing the temperature evolutions at three prescribed points (*i.e.*, $x = 0$ mm, $x = 31.75$ mm, and $x = 63.5$ mm) in Figs. 3(a)–3(c), the front temperature in the left and right end areas of each specimen was higher than the middle of it (Fig. 3). For instance, in Fig. 3(a), the temperature of points $x = 0$ mm and $x = 63.5$ mm rose to 241 °C and 234 °C. While the temperature increased to 223 °C at $x = 31.75$ mm. This trend can also be seen in curves of the front temperature, where the temperature increased dramatically in a short period of time. Then, the front temperature dropped to 226 °C and started to oscillate. After that, the front temperature increased to 238 °C. As mentioned before, this phenomenon is caused by the effect of the insulating boundary condition during the propagation process. Specifically, the front collided with the left end of the mold, in which the generated heat was trapped due to the insulating boundary condition, which led to the buildup of the exothermic heat and an increase in the temperature.

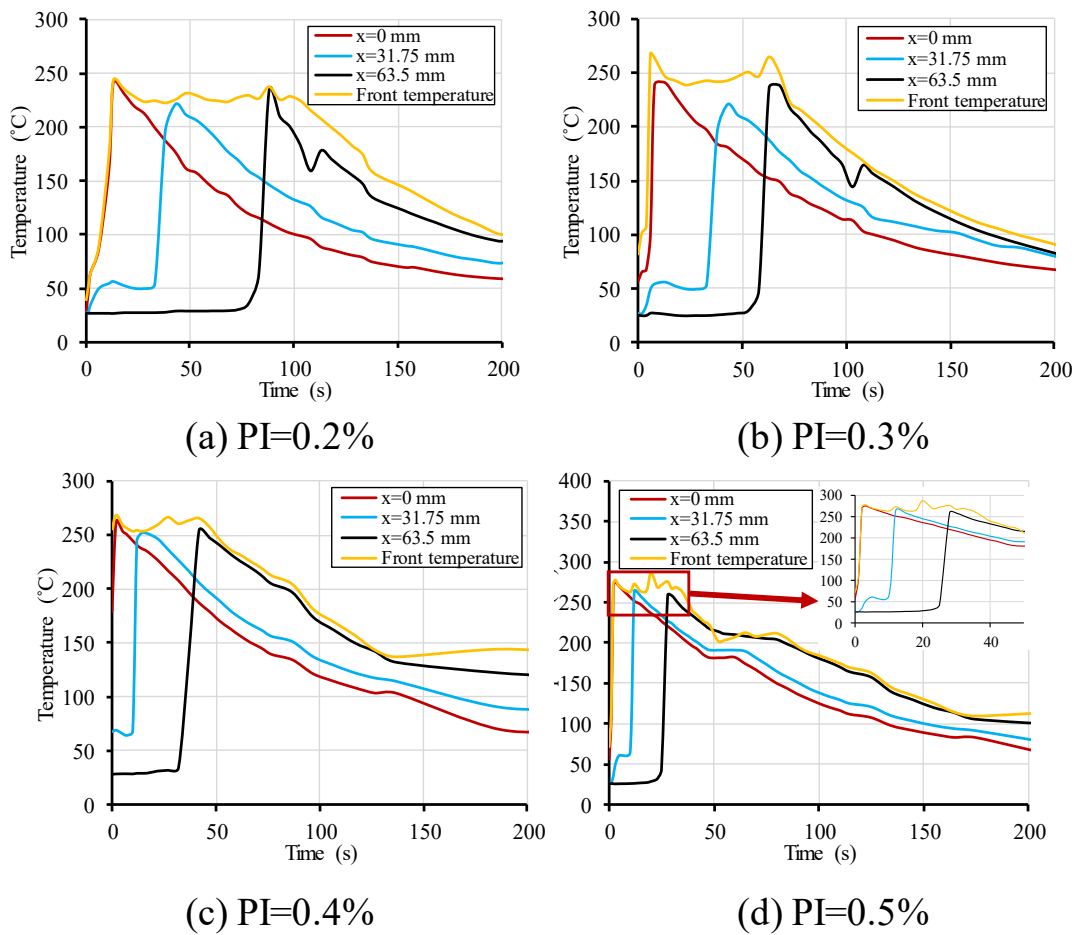


Figure 3. Evolution of temperature for different PI weight contents corresponding to three fixed points and curing front temperature.

From Figs. 3(c) and 3(d) (specimens with 0.4 wt% and 0.5 wt% of PI), due to the higher concentration of PI than other specimens, the front was initiated within a higher temperature range and in a shorter period of time than other specimens. Specifically, the initial temperatures of 0.4 wt% and 0.5 wt% of PI are on average

16.5 °C and 26.5 °C higher than those in 0.2 wt% and 0.3 wt% of PI. The initiation time of 0.4 wt% and 0.5 wt% of PI is 10 seconds lower than 0.2 wt% and 0.3 wt% of PI. This phenomenon caused the front to start with a higher velocity and initiation temperature on the top surface. This type of propagation pattern resulted in homogeneous front temperatures on the top surface, where the front temperatures oscillated around 256 °C and 261 °C (Figs. 3(c) and 3(d)), compared to other specimens, which had temperature peaks in the left and right regions. The thermal images, illustrated in Figs. 4(a)–4(c), show that the front propagation pattern had a sloped shape corresponding to a specimen with 0.4 wt% PI. As the curing front reached the left end of the mold, it started to propagate from the top through the bottom side of the specimen (Fig. 4(d)). In this way, the upper surface was polymerized with a higher velocity and cooled down faster than the region on the bottom side. This forms a wave-like pattern on the top surface (Fig. 5(a-1)), where

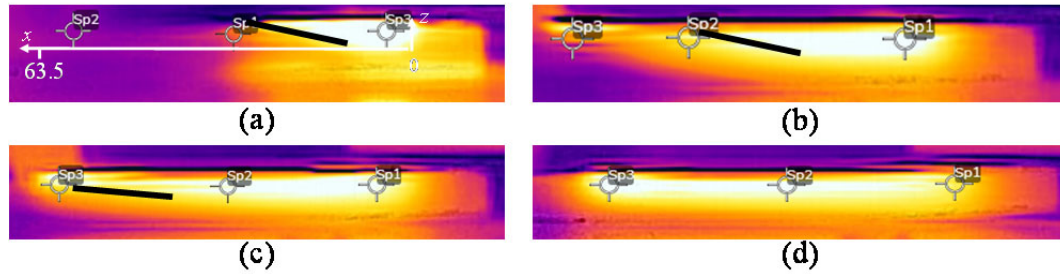


Figure 4. Front propagation pattern of specimen with 0.4 wt% of PI (side view).

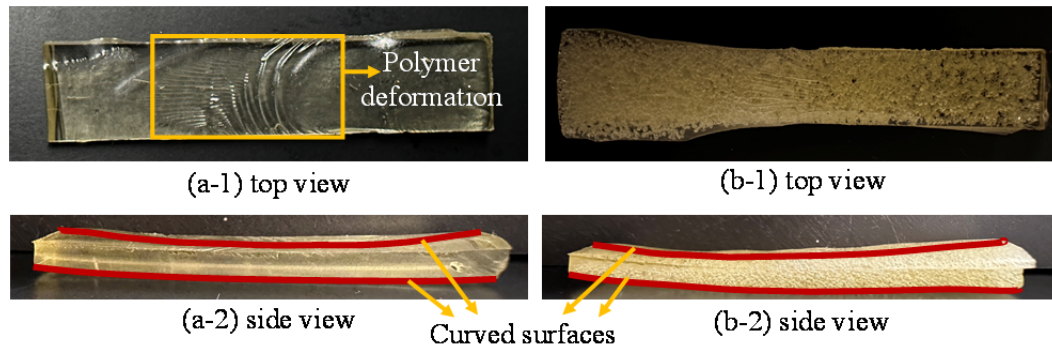


Figure 5. Frontal polymerization morphology corresponding to the specimens with (a) PI=0.4 wt% and (b) PI=0.5 wt%.

the propagation pattern exhibited a small slope (as indicated in black lines in Figs. 4(b), 4(c)). Additionally, the difference in top and bottom surface velocity caused the top surface to shrink, thereby resulting in curve surfaces (Fig. 5(a-2)). This behavior was observed in the specimen with 0.5 wt% PI (Fig. 5(b-2)). Additionally, the higher weight content of PI in this specimen resulted in thermal degradation and foaming due to the much higher exothermic heat generated inside the specimen during the polymerization process (Fig. 5(b-1)). The 0.5 wt% PI specimen had a maximum temperature of 278 °C, whereas the other specimens only had a maximum temperature of lower than 268 °C, as shown in Fig. 3.

The frontal polymerization characteristics for specimens with different weight contents of PI are summarized in Table II. Note that the average front velocity is calculated at three different locations. As can be seen, increasing the weight content of PI increases the front velocity and degree of cure. Comparing the temperature evolution and characteristics of each specimen revealed the relation between the effect of weight contents on the generated exothermic heat and FP characteristics. It is found that increasing the PI weight content from 0.2 wt% to 0.3 wt% significantly reduced the polymerization time and increased the front velocity and degree of cure, both, by two times. This difference in thermal behavior also resulted in different tensile properties of these specimens, as presented in Fig. 6. Increasing the weight content of PI improved the ultimate tensile strength and Young's modulus. From Fig. 6(a) and 6(b), the ultimate tensile strength and Young's modulus related to the 0.3

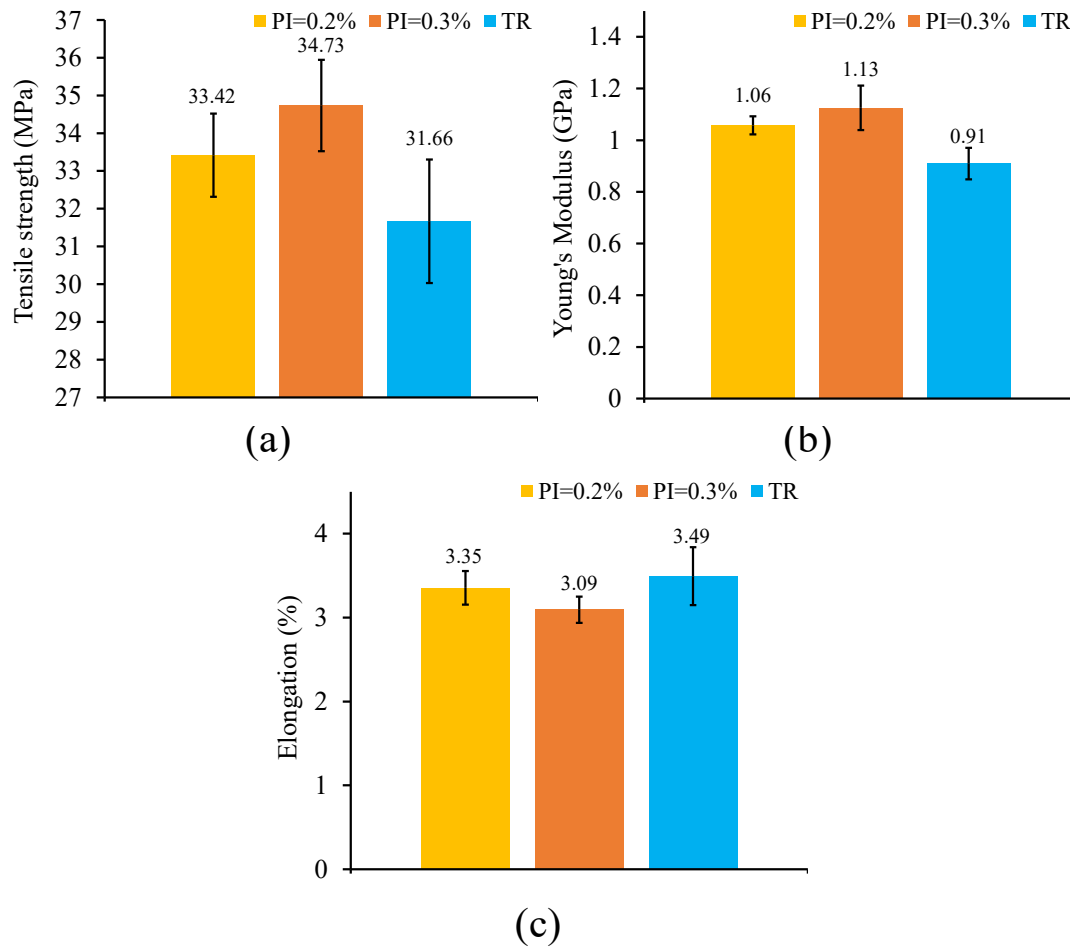


Figure 6. Comparative evaluation of the tensile properties in terms of (a) tensile strength, (b) Young's modulus, and (c) failure strain corresponding to specimens with 0.2 wt% and 0.3 wt% of PI and traditional specimen.

wt% PI specimen increase by 3.91% and 7%, respectively, when compared to the 0.2 wt% PI specimen. Moreover, increasing the PI weight content makes the

specimen more brittle. Specifically, the failure strain of the 0.3 wt% PI specimen is 0.16% lower than that of the 0.2 wt% PI specimen. Based on Table II, increasing the amount of PI to 0.4 wt% improved the front velocity and degree of cure. However, the polymerization process of this PI weight content caused the surface of the specimen to be curved. Due to this, it was not possible to conduct the tensile test on this specimen.

Based on Table II, the degree of cure improved from 40% to 93% by increasing the PI concentration from 0.2 wt% to 0.4 wt%. Comparing the degree of cure of 0.2 wt% with 0.3 wt% PI specimen showed that the degree of cure has been improved by two times. However, this increasing pattern was not observed when the 0.3 wt% PI specimen was compared with 0.4 wt% PI specimen where the degree of cure was increased from 80% to 93%, respectively. Increasing the PI concentration from 0.4 wt% to 0.5 wt% resulted in overcuring and foaming of the specimen.

Additionally, by comparing the tensile properties of oven-cured specimens with RICFP specimens, as shown in Fig. 6, the tensile strength of thermal-cured specimen is 1.76 (5%) and 3.07 MPa (9%) lower than 0.2 wt% and 0.3 wt% of PI specimens, respectively. The Young's modulus of the thermal-cured specimen is about 14 % lower than that of RICFP specimens. The failure strain for the thermal-cured specimen was higher than the frontal polymerized specimens.

When compared to the results reported by [18] corresponding to the FP characteristics of the neat epoxy resin specimen with the same silicone elastomer mold, it was revealed that the size of the specimen affected the FP process. Due to the smaller specimen dimensions in this study, for example, the front velocity of PI = 0.5 wt% (2.04 mm/s) is much higher than the velocity mentioned in [18] (0.99 mm/s). Additionally, the front temperature related to this study is about 20 °C higher than the temperature mentioned in [18]. Moreover, the dimension of the specimen also affects the degree of cure. Specifically, although 0.5 wt% of PI caused the specimen to be degraded and foamed in this study, the same PI weight content actually leads to 77 % of the degree of cure in the neat resin specimen of [18].

CONCLUSION

With the increasing demands towards the in-situ curing technique for additive manufacturing of thermoset-based FRPs, emerging the frontal polymerization gains incentive as a promising rapid-curing out-of-autoclave method in comparison with the thermal oven-curing fabrication method. This study aimed to investigate the frontal polymerization process of epoxy-based monomer with a dual-initiator configuration. The material system consisted of ECC epoxy resin, IOC-8 SbF₆ and benzopinacol as photo- initiator (PI) and thermal-initiator (TI). By fixing the weight content of the TI, neat ECC resin beam specimens with various weight contents of PI, *i.e.*, 0.2 wt% to 0.5 wt%, were fabricated. Then, the tensile standard specimens were cut out of beam specimens, whose degree of cure was characterized using FTIR and the temperature history was recorded by a thermal camera.

It was found that increasing the weight content of PI from 0.2 wt% to 0.5 wt% raised the average temperature from 220 °C to 270 °C. During the FP process, the temperature at the right and left ends of the specimen exhibited higher values than

the middle part due to the thermal insulation of the silicone mold at both ends. Thus, there were two temperature peaks at the left and right ends of each specimen. Additionally, increasing the PI concentration from 0.2 wt% to 0.3 wt% improved the FP characteristics, specifically the degree of cure, from 40% to 80%. Nevertheless, the FP characteristic did not considerably improve when the PI weight content was increased from 0.3 wt% to 0.4 wt%. Also, the front propagated from the top and bottom surfaces of the specimens with 0.2 wt% and 0.3 wt% of PI at the same time. The FP characteristics of a specimen with 0.3 wt% of PI, including the front velocity and the degree of cure, were two times higher than those of a specimen with 0.2 wt% of PI. However, the results for 0.4 wt% of PI showed that the front propagated from the top surface faster than the bottom side, which resulted in forming a curved shape of the specimen. This curved shape was also observed in the specimen with 0.5 wt% PI. Moreover, the high concentration of the 0.5 wt% PI caused the specimen to be degraded and foamed (*i.e.*, generated numerous bubbles within the epoxy specimen).

Additionally, the specimens with 0.2 wt% and 0.3 wt% of PI were tested to evaluate the effect of PI weight content on the tensile properties. The results showed that using 0.3 wt% PI increased the tensile strength and Young's modulus by 3.91% and 7%, respectively, compared to specimen using 0.2 wt% PI. However, the average elongation reduced from 3.35% to 3.09% by increasing the PI concentration. Moreover, the comparison of the tensile properties between oven-cured specimen and RICFP specimens showed that the frontal polymerization yielded 8% higher tensile strength and 14% higher Young's modulus on average, respectively. The polymerization time reduced from 15 hours to only 31-107 seconds.

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