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RESEARCH ARTICLE

Thiol-Acrylate Gel Systems For Frontal Polymerization

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ABSTRACT

A trithiol-triacrylate gel system for frontal polymerization was explored to establish the gelation time, shelf life, and frontal kinetics. The free-standing gels were created by triethylamine-catalyzed Michael addition of trimethylolpropane tris(3-mercaptopropionate) to trimethylolpropane triacrylate such that sufficient acrylate functional groups were left unreacted to allow free-radical frontal polymerization with the initiator 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane (Luperox 231). Systems with gelation times between 30 and 60 min that support frontal polymerization after up to 28 days of storage were achieved. The front velocity was found to depend on the 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane concentration. However, the amount of triethylamine, which was used to catalyze gel formation, did not significantly affect front velocity. The gel diameter and addition of milled carbon fiber (Zoltek px35) affected the front velocity. Cracks during frontal polymerization were reduced when Zoltek px35 was added to the formulation, which also increased the mechanical strength. Complex geometries of free-standing gels were successfully polymerized. This system is potentially useful in situations where molding and reshaping gels are required prior to frontal polymerization, as well as enabling the ability to examine how mechanical forces like stretching and compression can affect front kinetics.

1 | Introduction

Frontal polymerization (FP) is a process in which a localized reaction zone propagates through the coupling of thermal diffusion with the Arrhenius kinetics of exothermic polymerization. Frontal polymerization was first discovered by Chechilo and Enikolopyan with the free-radical polymerization of methyl methacrylate [1, 2]. Pojman "rediscovered" frontal polymerization with methacrylic acid in 1991 [3]. Frontal processes can be supported by a variety of polymerization mechanisms, such as ring-opening metathesis polymerization [4–6], free-radical polymerization [7–9], and cationic/anionic polymerization [10–13]. The rate at which the polymer front propagates, and the maximum front temperature are affected by parameters such as the selection of monomer, initiator/catalyst, and additives [14, 15].

Frontal polymerization has been identified as having the potential to be utilized in industries such as energy, infrastructure, aerospace, and automotive that use composites of highly cross-linked polymers that have been reinforced [16–19]. It can also be integrated into additive manufacturing, which opens new pathways of potential applications [20–24]. Frontal polymerization is often performed with neat monomers or monomers with inorganic fillers to modify the initial rheology and the mechanical properties of the product [25]. In this work, we created covalently bonded gels that could support frontal polymerization.

Thiols can be added to various groups such as isocyanates, epoxides, and acrylates through thiol-click reactions [26–29]. Michael's addition of thiols to acrylates can be classified as a type of thiol-click reaction where bases, usually amines, are used as catalysts [30–32]. The use of thiol and ally ether as well as multifunctional acrylates have been shown to produce polymerization fronts by a free-radical process with observable spin modes, which are nonplanar modes of propagation [30, 33].

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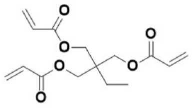
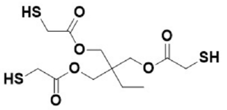
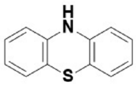
Binici et al. investigated the possibility of creating gels via the Michael addition of thiols to acrylates followed by free-radical polymerization by having an acrylic-to-thiol ratio larger than one. The thiol-acrylate solution contained a tertiary amine to catalyze the Michael addition and Luperox 231 to generate radicals for the frontal polymerization of the excess acrylate when heat is applied. The formation of gel was observed when the thiol was almost completely consumed in the Michael addition. A front was initiated by exposure to UV light that reacted with a photoinitiator injected in the center of the gel. A spherically propagating front was created that exhibited complex fronts with "spin modes" on the surface of the expanding front [30, 34].



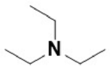
TMPTA



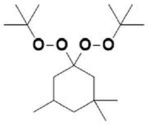
TT1



Phenothiazine



TEA



Luperox 231

We used the same formulation as Binici et al. to ascertain the front kinetics dependence on the concentration of the various chemical species used and examine the stability of the gels and ways to improve the mechanical properties of the products formed. Various constituents of the formulation were investigated to determine their influence on the behavior of the front and the structural integrity of the products. To increase the shelf life of the gels, inhibitors were added. To reduce cracking during polymerization, milled carbon fiber was incorporated, which also enhanced the mechanical properties due to its high modulus and tensile strength [35, 36].

Other systems using dicyclopentadiene (DCPD) have been shown to form a gel intermediate that can undergo frontal ring-opening metathesis polymerization. The DCPD system has a pot life of less than 30 min [4, 37, 38] and up to 30 h when inhibitors of the alkyl phosphite family are incorporated [39]. The thiol-acrylate system investigated in this report has been shown to have a pot life of up to 28 days.

The ability to form free-standing flexible gels potentially allows for molding and reshaping before curing via frontal polymerization along with the ability to suppress bubble formation during frontal polymerization with gas-producing radical initiators [19, 30]. Free-standing gels can also allow the examination of how factors like mechanical forces can affect frontal polymerization [38], which is not possible for neat monomers or monomers with fillers.

2 | Experimental

2.1 | Materials

Trimethylolpropane triacrylate [TMPTA] was purchased from Allnex. Trimethylolpropane Tris(3-mercaptopropionate) [TT1] from TCI America and triethylamine [TEA] from VWR chemicals were purchased from VWR international. 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane [Luperox 231] and phenothiazine were purchased from Sigma–Aldrich and Zoltek px35 (milled carbon fiber with 150 μm length × 7.2 μm diameter) was procured from Zoltek Corporation. All chemicals were used as received.

2.2 | Preparing Thiol-Acrylate Gel by a Michael Addition of TMPTA and TT1

A 36 g of TMPTA was weighed in a polypropylene cup and varying concentrations in parts per hundred resin (phr) of Luperox 231 (4–30 phr) was added. A 17 g TT1 was weighed into a second polypropylene cup, and TEA was added. The contents in the two cups were then mixed and stirred in an ice bath using a magnetic stirrer for 3–5 min.

The resulting mixture was then transferred into test tubes or silicone molds of desired geometries (like a fleur-de-lis mold used to obtain the shapes in the graphical abstract) and allowed to gel in an ice bath for about 3–5 h to form free-standing gels. The formulation changed from a colorless free-flowing mixture to a white gel. The gel was then allowed to sit for 24 h after mixing to allow complete gelation and equilibration to room temperature. The resulting gel was flexible and could be folded, as illustrated in Figure 1. The putative 3:1 mol ratio of TMPTA:TT1 was used because an inadequate amount of TMPTA produced a rigid gel or solid that did not support a front and having too much TMPTA caused the formation of a viscous liquid instead of a free-standing gel.

2.3 | Frontal Polymerization of Thiol-Acrylate Gel

The gels were removed from the molds or test tubes by carefully breaking the test tube with a mallet and peeling off glass shards. The free-standing gels were then stored in Ziplock bags at room temperature between 20°C and 24°C. A soldering iron was heated to above 200°C and used to initiate the front after touching the base of the gel for 30 to 60 s. The front was tracked with a SONY HDR-CX405 Handycam camcorder with the help of a ruler as shown in Figure 2. A Seek thermal (LW-AAA) imaging camera was used to track front propagation for formulations containing Zoltek px35 (milled carbon fiber) due to the very subtle visual difference between the gel and polymer. The video from the imaging camera was overlayed with a virtual ruler that replicated the actual length of the sample. The front velocity was then calculated from the slope of the front position versus time. Maximum front temperature was measured using a BENETECH GM1312 thermometer (with an error margin of ±0.1% + 0.6°C) by inserting the thermocouple wires into the gels before frontal polymerization was carried out. Three independently prepared cylindrical samples for each formulation were analyzed.

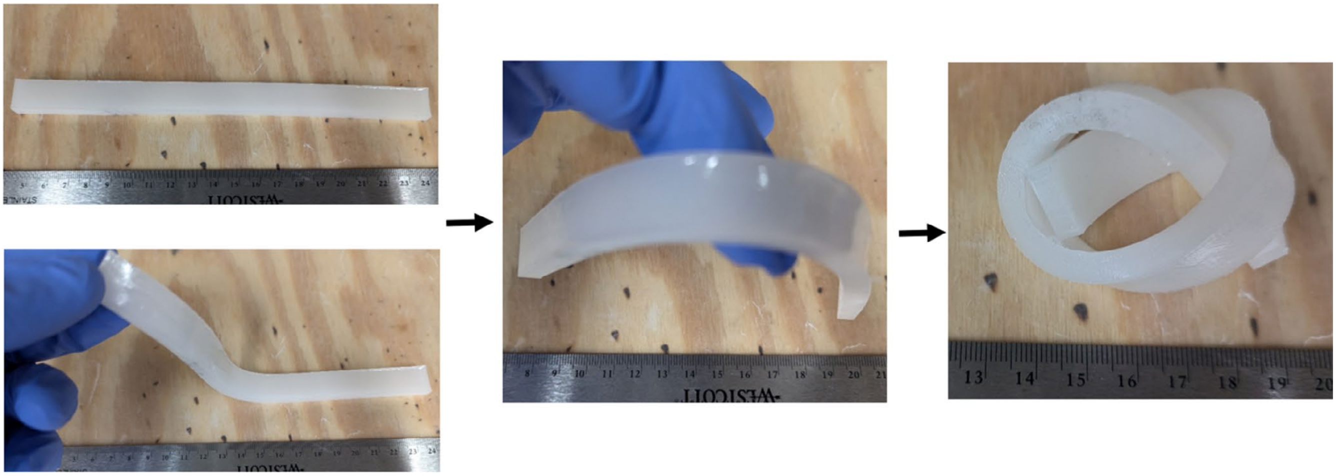


FIGURE 1 | The thiol-acrylate gel was sufficiently flexible that it was easily folded before frontal polymerization. The ruler indicates the length in centimeters.

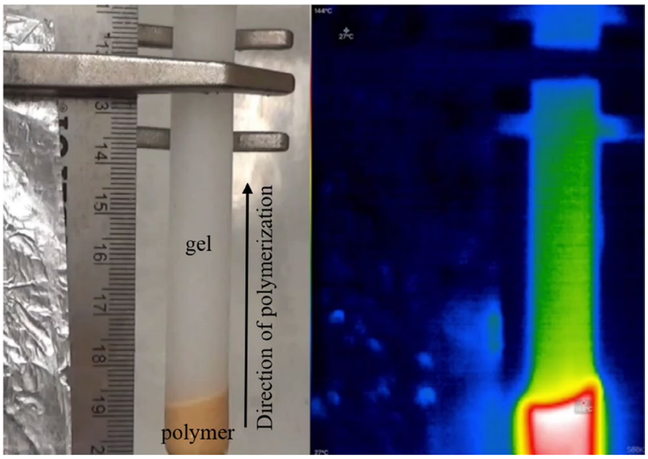


FIGURE 2 | Frontal polymerization of free-standing gel. (the ruler indicates the distance in centimeters). The left image was from the digital camera, and the right image was from the thermal imaging camera.

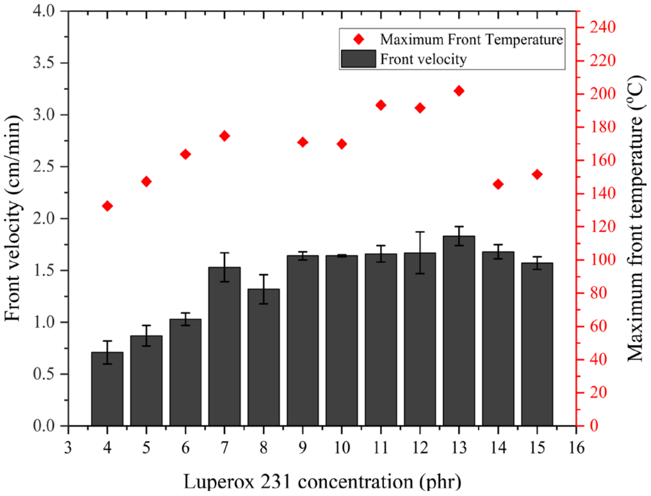


FIGURE 3 | Front velocity vs. Luperox 231 concentration and maximum front temperature of formulation with a 3:1 mol ratio of TMPTA:TT1 and 2.5 phr TEA.

2.4 | Flexural Testing

Flexural testing was performed using an Instron 5969 universal testing machine. Samples for testing with sizes according to ASTM D790 were produced in silicone molds. The crosshead speed was calculated based on the ASTM standard and the thickness and width of each sample. The support span length was set at 50 mm.

3 | Results And Discussion

3.1 | Dependence of Front Velocity on Luperox 231 Concentration

The dependence of front velocity on Luperox 231 concentration was examined by preparing formulations with Luperox concentrations from 4 to 15 phr, maintaining the TEA concentration at 2.5 phr. The front velocity, as expected, was found to increase as the concentration of Luperox 231 was increased [40] until it reached its maximum around 13 phr, as shown in Figure 3. Such a maximum was typically observed for free-radical frontal polymerization [40–43]. The front velocity gradually decreased after 13 phr because of a possible dilution effect of Luperox 231 tending to be greater than its contribution to front velocity and/or termination of polymerization by radicals from the initiator. Increases in maximum front temperature tracked by a thermocouple were also found to correlate with front velocity (Figure 3). It was also observed that as the concentration of Luperox 231 was increased, the frontal polymerization products varied in color from a slightly translucent orange color to an opaque yellow (Figure 4). This may result from phase separation occurring as more Luperox 231 was added to the formulation due to the gel and the liquid Luperox 231 existing in different phases.

3.2 | Study of Front Velocity as a Function of Storage Time

When fronts were run after some time of storage at room temperature between 20°C and 24°C, it was observed that there was a decrease in front velocity as the length of days of storage increased with formulations containing a lower amount of Luperox 231 decreasing more sharply than those containing higher concentrations of Luperox 231, as can be seen in Figure 5. This may be a result of background polymerization of the excess acrylate groups during storage [14], which decreases the amount of reactive acrylate groups. However, as Luperox 231 concentration was increased there were more reactive radicals to counteract this decrease.

We observed an unusual structure in the cross section of the polymerized products (Figure 6). There were two distinct areas within the polymer, an outer orangish-yellow layer, and an inner yellow layer. Upon examination of gels stored after more than 7 days, it was noted that the inner part of the gel was harder than the outer section. This is because TMPTA contained, an aerobic inhibitor, methyl ethyl hydroquinone (MEHQ), which likely inhibited background polymerization of the outer layer more effectively than the inner layer because of easier access to atmospheric oxygen by the outer layer. This also explains the delamination or peeling effect observed when gels stored for more than 14 days were frontally polymerized, as shown in Figure 7, because of the difference in composition in the inner and outer layers.

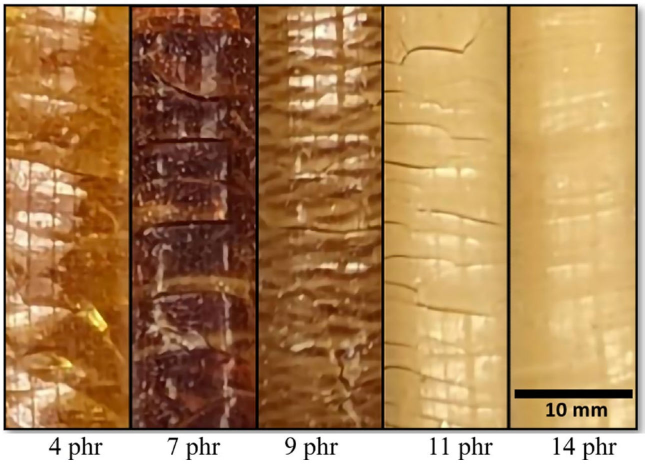


FIGURE 4 | Variation in the appearance of the polymer as a function of Luperox 231 concentration. Notice how the color of the polymer changes from translucent orange to opaque yellow.

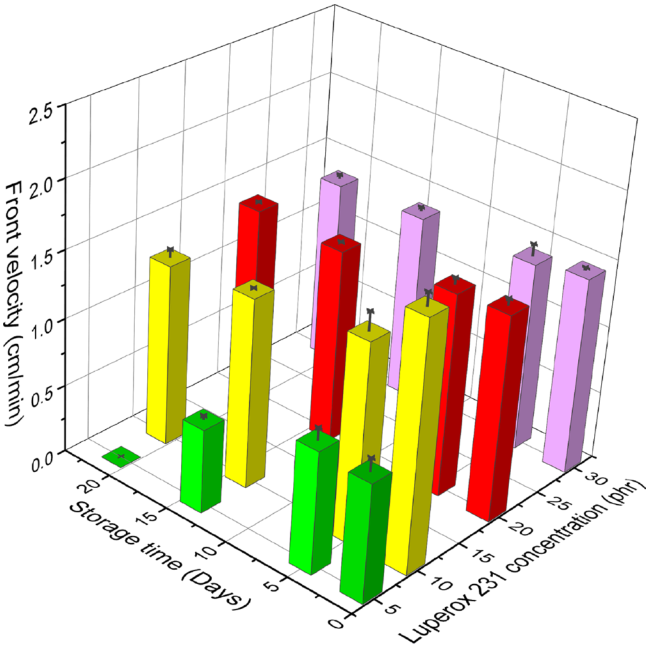


FIGURE 5 | Front velocity vs. storage time and Luperox 231 concentration of formulations containing a 3:1 mol ratio of TMPTA:TT1 and 2.5 phr TEA.

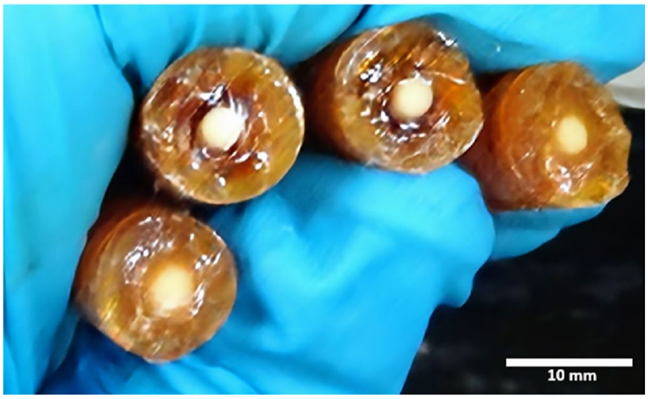


FIGURE 6 | Image of the cross section of the polymerized gels. Notice the difference in the middle vs. the outer layers.

FIGURE 7 | Peeling observed from different positions around the same polymerized sample, with MHQ as the inhibitor.

FIGURE 8 | Cross section of polymer containing phenothiazine.

FIGURE 9 | Sample polymerized with no phenothiazine (left) vs. those with 0.5 phr phenothiazine (right). (TMPTA used in all samples contained about 250 ppm of MEHQ from the manufacturer). Notice that peeling is not observed in the samples containing phenothiazine.

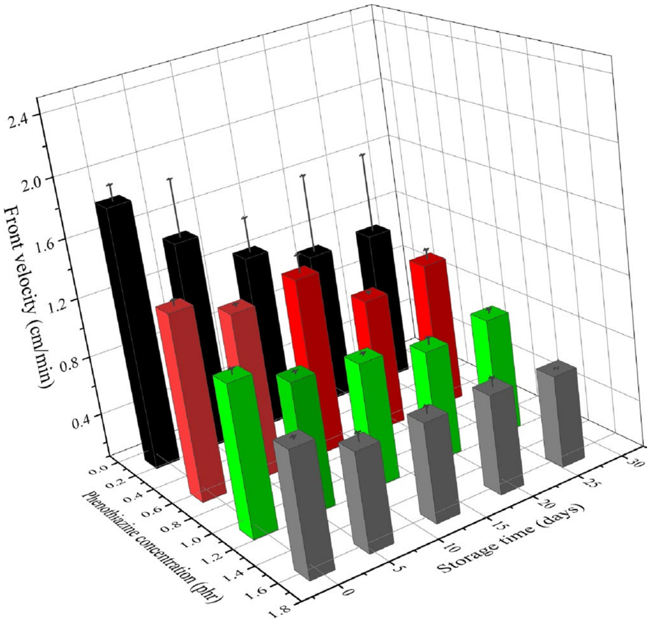


FIGURE 10 | Front velocity as a function of phenothiazine concentration and storage time of formulations with a 3:1 mol ratio of TMPTA:TT1, 5 phr Luperox 231, and 2.5 phr TEA.

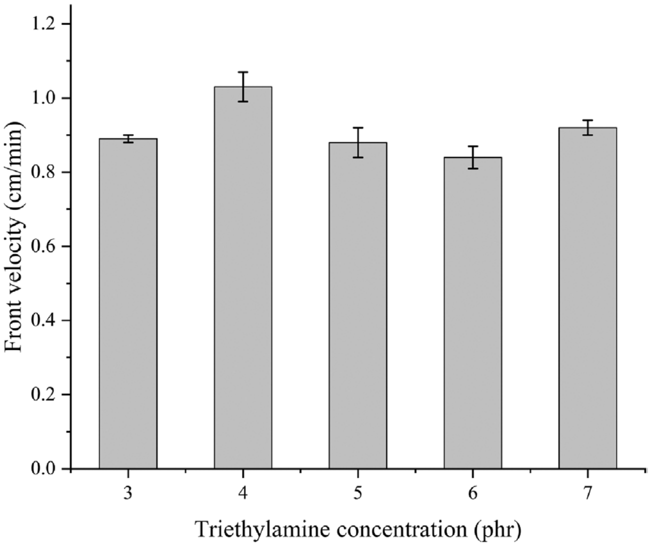


FIGURE 11 | Front velocity vs. triethylamine concentration after 24 h of storage. Formulations contain a 3:1 mol ratio of TMPTA:TT1 and 5 phr Luperox 231.

The peeling effect was mitigated by the addition of the anaerobic inhibitor phenothiazine [44]. The addition of phenothiazine allowed a more uniform inhibition of the background polymerization and prevented the peeling phenomenon, as shown in Figures 8 and 9. However, the addition of phenothiazine led to a reduction of the front velocity but was able to retain more than 70% of its day 1 front velocity after 28 days of storage as compared to the formulation without the phenothiazine, which retained less than 60% of its higher front velocity (Figure 10).

3.3 | Dependence of Front Velocity on Triethylamine Concentration

The concentration of triethylamine decreased the gelation time, which was expected because increasing catalyst concentration increases the rate of reaction. The triethylamine concentration did not significantly affect the front velocity, as shown in Figure 11. The polymer became darker as the TEA concentration was increased as the coloration may be due to the oxidation of triethylamine (Figure S1 in supplementary information).

3.4 | Dependence of Front Velocity on Sample Diameter

To determine how the diameter of the gel affected the front velocity, four test tubes were used to generate gels with diameters of 8, 13, 16, and 30 mm. The front velocity increased with increased gel diameter (Figure 12). As the diameter of the gel increased, the surface area to volume ratio decreased, which reduced heat lost to the environment therefore increasing the front velocity [45].

3.5 | Effect of Adding Zoltek px35 to Formulation

Zoltek px35 (milled carbon fiber) was added to the formulation to reduce cracks generated after frontal polymerization and also improve the mechanical properties [46]. As shown in Figure 13,

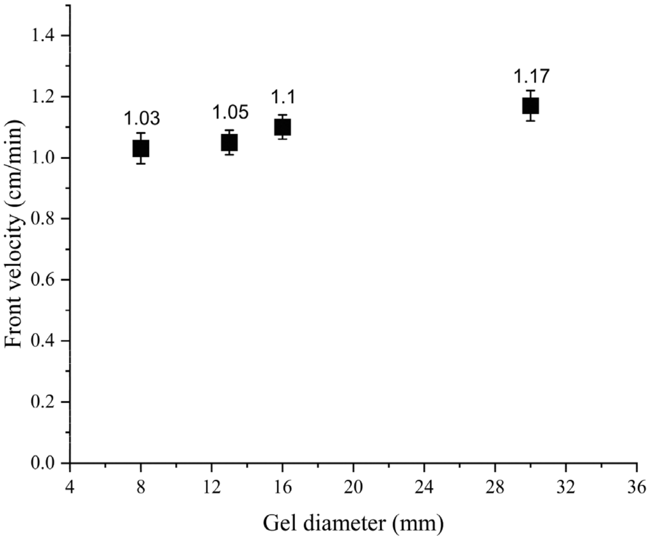


FIGURE 12 | Front velocity vs. gel diameter (5 phr Luperox 231).

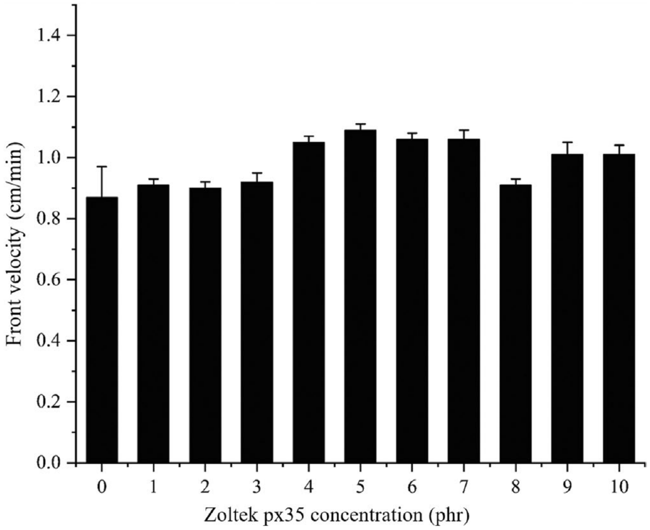


FIGURE 13 | The dependence of front velocity on Zoltek px35 loading for formulation prepared with a 3:1 mol ratio of TMPTA:TT1, 5 phr Luperox 231, and 2.5 phr TEA.

the addition of Zoltek px35 to the formulation increased the polymerization front velocity but after adding about 5 phr of Zoltek px35any additional increase in Zoltek px35 loading did not lead to a further increase in front velocity but a decrease in front velocity. Zoltek px35, which is milled carbon fiber, is a conductor of heat [47, 48], which increased thermal transport and thus increased the front velocity. The front velocity was maximum at 5 phr and decreased after 5 phr due to the ability of Zoltek px35to absorb heat from the reaction front [49, 50] and a possible increase in heat loss from increased rate of conduction of heat to the surroundings. The addition of Zoltek px35 (carbon fiber) also made the gels stiffer and stronger as can be seen from the stress vs. strain curve in Figure 14. The addition of 5phr Zoltek px35 (carbon fiber) increased the flexural stress capacity by more than 8 times as compared to samples not containing Zoltek px35.

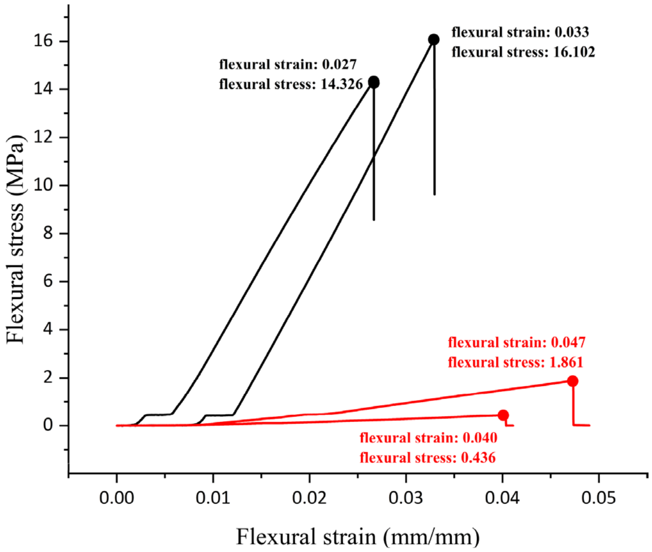


FIGURE 14 | Flexural stress vs. strain of polymerized gels (5 phr Zoltek px35 (carbon fiber) was used in gels containing Zoltek px35 (carbon fiber) and all samples contained a 3:1 mol ratio of TMPTA:TT1, 2.5 phr TEA and 5 phr Luperox 231). The black lines represent samples containing Zoltek px35, and the red lines represent samples without Zoltek px35.

4 | Conclusion

Free-standing thiol-acrylate gels that support frontal polymerization up to 28 days after storage at room temperature were successfully formulated, with gelation time ranging from 30 to 60 min. Front velocity was shown to be correlated with Luperox 231 concentration. Concentrations of TEA between 3 and 7 phr had no significant effect on front velocity. Front velocity was affected by changing the gel diameter and adding Zoltek px35 (carbon fiber). When Zoltek px35 (carbon fiber) was added to the formulation, the cracks created during frontal polymerization were reduced, while the polymer strength was increased. Phenothiazine was able to decrease front velocity loss during storage, indicating a decrease in homo-polymerization.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.