Frontal Cationic Curing of Epoxy Resins

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ABSTRACT: We studied the frontal curing of trimethylolpropane triglycidyl ether (TMPTGE) using two BF_3-amine initiators and two fillers, kaolin and fumed silica. In the case of kaolin, the range of concentrations allowing for frontal polymerization to propagate was dependent on its heat absorption effect whereas in the case of silica it was a consequence of the rheological features of this additive. However, for both systems the velocity and front temperature show the same trends; in all cases front velocities were on the order of 1 cm/min with front temperatures about 200 °C. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 2000–2005, 2010

KEYWORDS: cationic polymerization; composites; curing of polymers; epoxy resins; frontal polymerization

INTRODUCTION Thermal frontal polymerization (FP) is a localized reaction that propagates through the coupling of thermal diffusion and the Arrhenius dependence of an exothermic polymerization reaction. The result is a localized thermal reaction zone that then propagates through the reactants as a thermal wave.[1–5] A comprehensive bibliography of frontal polymerization research can be obtained at the website listed in reference.[6] Most of the FP systems studied to date have been based on free-radical chemistry.[6–19] Free-radical systems have the advantage of rapid reaction at their adiabatic reaction temperature but low rate of reaction at room temperature. They were ignited by UV[9,20–23] or thermal radiation.[24–26] Frontal curing of epoxy–amine systems was first studied by Arutiunian et al.[27] and Surkov et al.[28] and later Mariani et al.[29] modeled the system. Chekanov et al. studied FP of amine–epoxy systems using diglycidyl ether of bisphenol A (DGEBA) as the epoxy.[30] FP with amine-cured DGEBA and clay was studied by Mariani et al.[31] Using a cationic photoinitiator along with a benzoyl peroxide, thermal FP with an epoxy resin was achieved using UV light to ignite.[23] Crivello also considered such hybrid free-radical/cationic frontal photopolymerizations.[32] Crivello developed photoactivated cationic ring-opening frontal polymerizations of oxetanes.[33–37]

The short pot life of amine-cured epoxy systems is a problem. We would like to have a system that was premixed and would remain unreacted for weeks if not months. Latent cationic catalysts provide some hope but if the catalyst and resin will not react at room temperature for a long time, then a high curing temperature is required. Pojman et al. studied a binary frontal polymerization system that contained a BCl_3-amine complex.[38] We chose two BF_3-amine catalysts that have pot lives of several hours and would readily support frontal curing. To suppress buoyancy-driven convection, we added filler. We used kaolin (Polygloss 90®), a typical hydrous alumino-silicate clay[39] and fumed silica (Aerosil). We studied how the front velocity and front temperature were affected by the amount of catalyst and the amount of filler.

EXPERIMENTAL

Materials

The BF_3-amine initiators (Leecure B-110 and B-950) were obtained from Leepoxy. B-110 and B-950 have a reported gel time at 80 °C of 5 and of 11 min, respectively. Fumed silica (Aerosil) was obtained from US Composites Aerosil. The kaolin was the clay PolyGloss 90® from Huber. Trimethylolpropane triglycidyl ether (TMPTGE) was used as received from Aldrich.

Preparation of Reactant Mixture

In a typical run, a mold made of wood (50 mm × 20 mm × 20 mm) was loaded with a 10 g of TMPTGE and the appropriate amount of initiator calculated in terms of phr (weight parts per hundred resin); these last components were thoroughly mixed to obtain a homogeneous mixture. The proper amount of filler was added to this, and the resulting mixture was scrupulously mixed again. The mold was kept open because our focus was to create a system as much as possible similar to real-world applications. Anyway, the high viscosity of the system prevented significant surface variation.
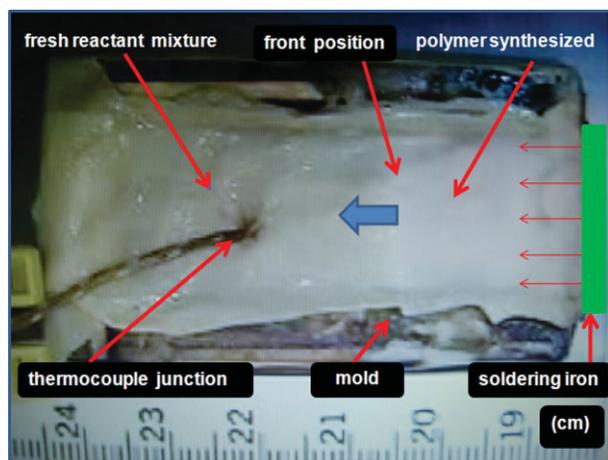
FIGURE 1 Schematic and visual image of a propagating front of TMPTGE with B-110 as initiator in the presence of fumed silica as filler.

FP Runs

FP reactions were triggered by heating the short side of the mold with a hot soldering iron until the formation of a horizontal traveling front.

Velocity and Temperature Measurements

Front temperature was measured with a 450-AKT OMEGA thermometer with a K-type thermocouple (30 AW) wire with glass braid insulation. The junction was located at 35 mm from the heating ignition side and was immersed at about 0.5 cm from the upper surface of the mixture. Front position was monitored by a digital thermocouple reader and recorded as a function of time. The frontal velocities (V_f) were determined by measuring the front position as a function of time. Some expansion occurred and so front velocities were corrected for this expansion. For example, if the sample expanded 10% during the experiment, it was taken as 90% of the measured value. The mixtures showed a pot life of more than 4 h regardless of the initiator or the filler used.

All experiments were performed three times and the results averaged.

RESULTS AND DISCUSSION

Preliminary Experiments: Effect of Catalyst Concentration on FP

Some preliminary experiments were performed to evaluate the critical reaction conditions, that is, the range of relative amounts of initiators (B-110 or B-950),[30] filler (fumed silica, 10 phr), and monomer (TMPTGE, 10 g) for FP to occur. Figure 1 presents an image of a propagating TMPTGE polymerization fronts. The interface between polymer and unreacted monomer can be barely seen. The dark gray zone shows the reactant mixture while the light green zone is the polymer. Front propagation occurred at a constant velocity by conversion of the monomer to poly-TMPTGE with almost no formation of bubbles.

The maximum temperature (T_{max}) reached by the traveling front and V_f are considered the two main parameters to be checked during an FP experiment. The latter is easily calculated by plots such as that depicted in Figure 2, in which the position of the front as a function of time for a typical FP run is reported. As can be seen, in this example as well as in all syntheses reported in this work, experimental data are well fitted by a straight line, thus indicating that front propagates at a constant velocity, a feature typical of many FP systems if no other simultaneous reactions are occurring.

We determined the T_{max} and V_f as functions of initiator concentration (5, 10, 15 phr) while keeping the amount of fumed silica fixed at 10 phr [Fig. 3(a,b)].

The larger the amount of initiator, the higher were T_{max} and V_f. Moreover, it was found that regardless of the initiator used, formulations containing less than 5 phr of initiator did not frontally polymerize. On the contrary, a very fast FP takes place by increasing the amount of initiator. These findings suggest that FP could also be performed using larger amounts of inert filler. Moreover, by comparing V_f data, it should be also pointed out that B-110 exhibits greater reactivity than B-950 under these reaction conditions [Fig. 3(b)]. The following discussion will deal with the effect of the relative amounts of the reaction mixture components in the range of 5–15 phr of initiators and of 5–80 phr of filler.

Effects of Inorganic Fillers
#### Experiments with B-110 and Fumed Silica

Taking into consideration our preliminary results, several FP tests were performed to investigate the effect of silica in the presence of B-110.

The experimental T_{max} and V_f data relating to three different concentrations of B-110 (5, 10, and 15 phr) in the range of 0–20 phr of fumed silica are reported in Figure 4.

With 15 phr B-110, the amount of silica was varied from 0 to 20 phr. Indeed, at larger contents, the mixture became too viscous to be easily handled. T_{max} and V_f, shown in Figure 4,
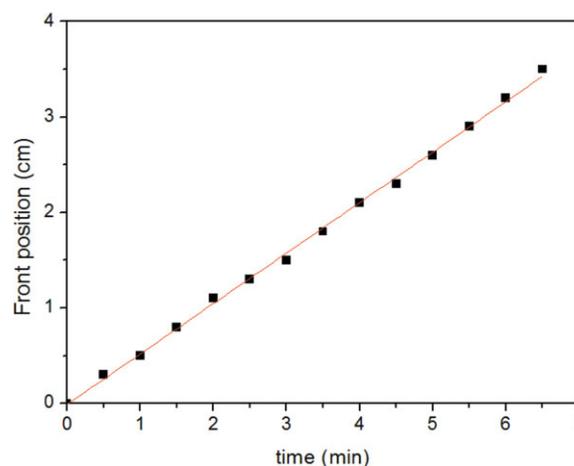
FIGURE 2 Front position versus time for a typical run of TMPTGE with B-110 (5 phr) in the presence of fumed silica (5 phr). V_f is represented by the slope of the fitted straight line.
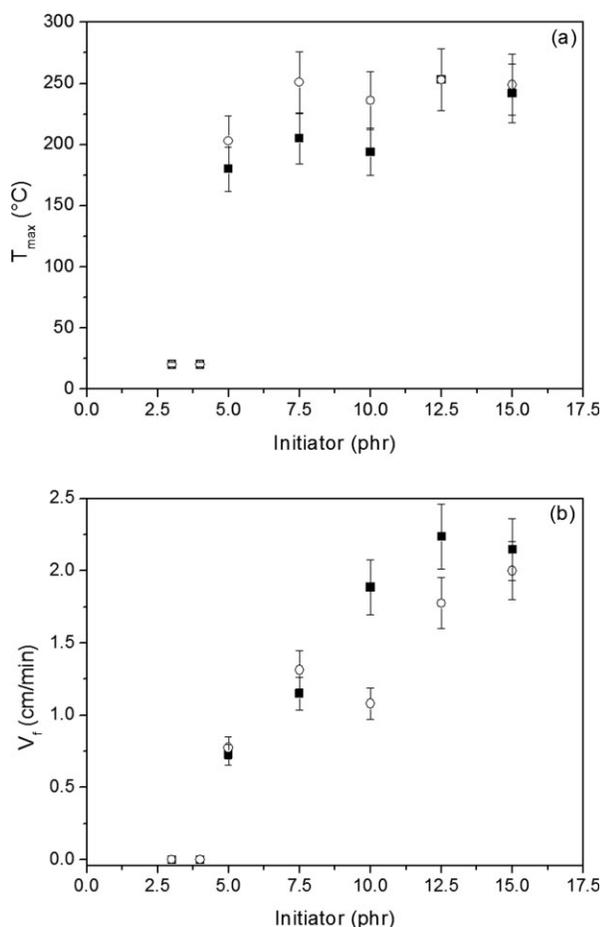
FIGURE 3 Front temperature (a) and front velocity V_f (b) as functions of initiator concentration (■, B-110; □, B-950) in the presence of fumed silica (10 phr).

generally decrease as the content of filler is increased. In particular, temperature goes from 270 °C (0 phr of filler) to 216 °C (20 phr of filler) [Fig. 4(a)]. Likewise, V_f decreased from 3.3 (0 phr of filler) to 1.3 cm/min (20 phr of filler) [Fig. 4(b)].

Similar decreasing trends were observed also for lower B-110 concentrations. Namely, when B-110 was equal to 10 phr, T_{max} and V_f ranged from 252 °C and 2.5 cm/min (in absence of filler) down to 204 °C and 1.1 cm/min (when the content of fumed silica was equal to 20 phr). It should be noticed that, as a consequence of an excessive heat loss, when the concentration of B-110 was 5 phr, FP occurred only in the range from 0 to 15 phr silica. In this range, T_{max} and V_f decreased from 208 to 167 °C, and from 1.2 to 0.4 cm/min, respectively. Such trends are easily explainable by considering that the increase of fumed silica content results in larger amounts of absorbed heat.[27]

Experiments with B-110 and Kaolin Clay

The effect of kaolin clay on the same reaction mixture as described above, in which B-110 was used as the initiator (Fig. 5), was studied. It was found that this filler influences

viscosity much less than fumed silica. This allowed the preparation of TMPTGE/Kaolin clay mixtures able to sustain FP fronts having filler contents up to 80 phr, at least for the largest initiator concentration (15 phr).

However, when B-110 was present at a concentration of 10 phr, the content of kaolin clay could not exceed 55 phr, while when the lowest concentration of B-110 was used (5 phr), FP occurred only for amounts of kaolin clay up to 20 phr. With 15 phr of B-110, V_f ranged from 3.3 cm/min in absence of filler to 0.8 cm/min at 80 phr of kaolin clay [Fig. 5(b)]. However, in the same range, T_{max} decreased from 270 to 184 °C [Fig. 5(a)]. Moreover, the use of 5 phr resulted in the highest V_f (4.1 cm/min).

When 10 phr B-110 was used, T_{max} and V_f were lower than those found with the highest initiator concentration; namely, they ranged from 252 °C and 2.5 cm/min in absence of kaolin clay to 179 °C and 0.6 cm/min when the amount of this filler was 55 phr. This trend was confirmed by further decreasing the initiator amount down to 5 phr. At this concentration, T_{max} ranged from 206 to 167 °C and V_f from 1.2 to 0.6 cm/min, at 0 and 20 phr of filler, respectively.
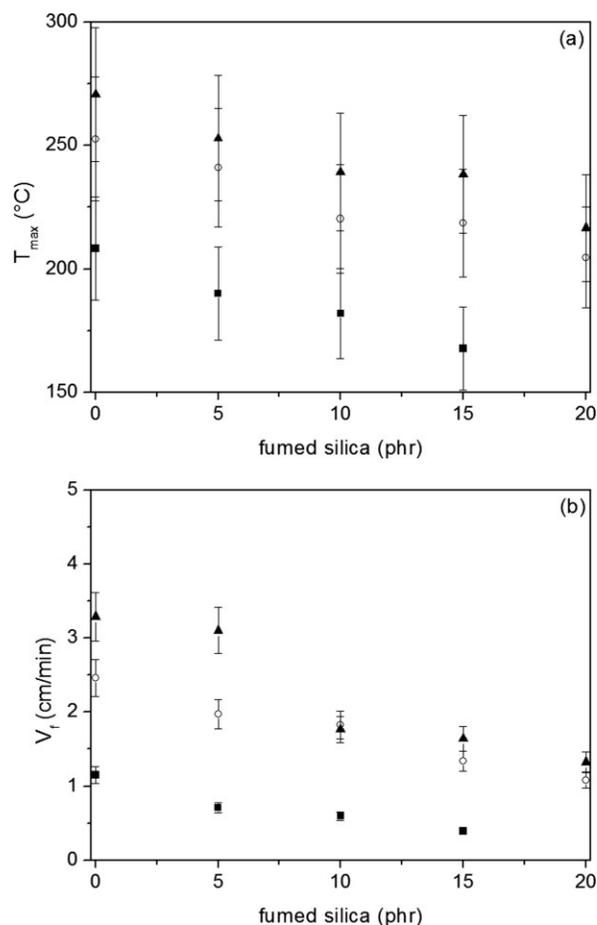
FIGURE 4 Front temperature (a) and front velocity (b) as functions of the amount of fumed silica for three different B-110 concentrations (■, 5 phr; ○, 10 phr; ▲, 15 phr).
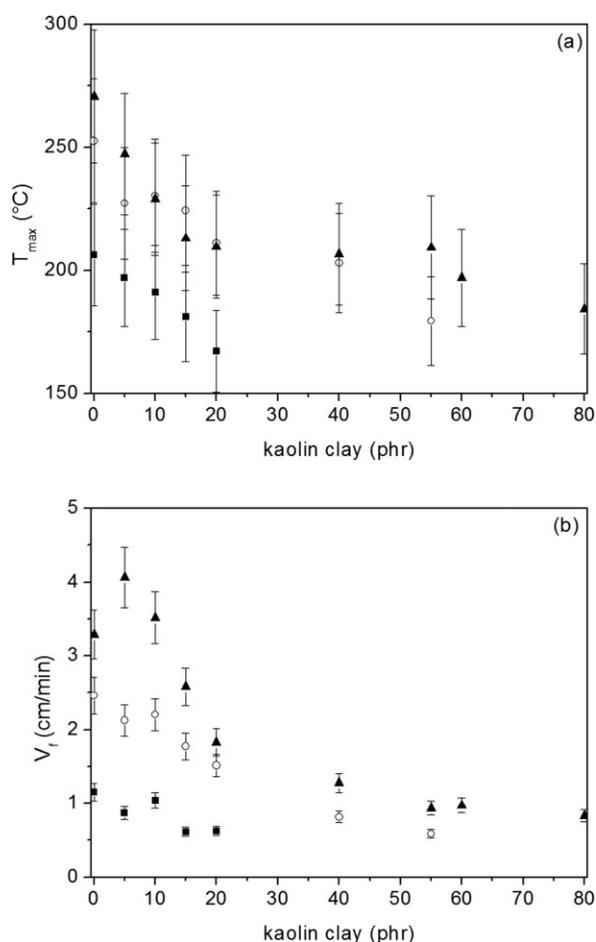
FIGURE 5 Front temperature (a) and front velocity (b) as functions of the amount of kaolin clay for three different B-110 concentrations (■, 5 phr; ○, 10 phr; ▲, 15 phr).

The existence of the frontal mode was related to the initiator and filler loading. Indeed, B-110 at 15 phr was able to support FP even with 80 phr kaolin clay. However, 10 and 5 phr of B-110 allow for FP to self sustain only up to 55 and 20 phr of kaolin clay, respectively [Fig. 5(a,b)].

Experiments with B-950 and Fumed Silica

Front velocity and front temperature as functions of the amount of fumed silica are plotted in Figure 6(a,b) for three different B-950 concentrations (5, 10, and 15 phr).

It was found that, independent of the concentration of B-950, FP occurred in the whole range of fumed silica content up to 20 phr. As already stated, larger loady of fumed silica resulted in mixtures too viscous to use, which for this reason were not used. As can be seen in Figure 6(a,b), when the amount of B-950 was equal to 5 phr, both T_{max} and V_f monotonically decrease as fumed silica increases from 0 to 20 phr. Namely, in this interval, they range from 251 to 163 °C and from 2.0 to 0.4 cm/min, respectively. However, for B-950 concentration equal to 10 and 15 phr T_{max} trend has a maximum, whereas V_f is represented by an even more irregular behavior that cannot be easily explained.

Experiments with B-950 and Kaolin Clay

The effect of the use of B-950 as the initiator of mixtures containing different concentrations of kaolin clay was also investigated. It was found that FP occurs for kaolin clay contents up to 20, 40, or 60 phr for concentrations of B-950 of 5, 10, or 15 phr, respectively, [Fig. 7(a,b)]. Also, in this case, the higher initiator concentration allows higher amounts of kaolin clay with front propagation.

Both T_{max} and V_f trends shown in Figure 7(a,b) are non-monotonic. We suppose the velocity and front temperature exhibit a maximum at 10 phr kaolin clay because convection is suppressed, which cools the front. However, analogously to what reported for the previous systems, in the explored interval T_{max} ranges from ~250 to 176 °C, and V_f from 3.5 to 0.5 cm/min as the amount of filler raises, thus indicating that front velocity is much more dependent than T_{max} on the reaction mixture composition.

CONCLUSIONS

Frontal curing of a triepoxy resin was achieved using two different BF$_3$-amine initiators in the presence of various amounts of two fillers: fumed silica and kaolin clay. The
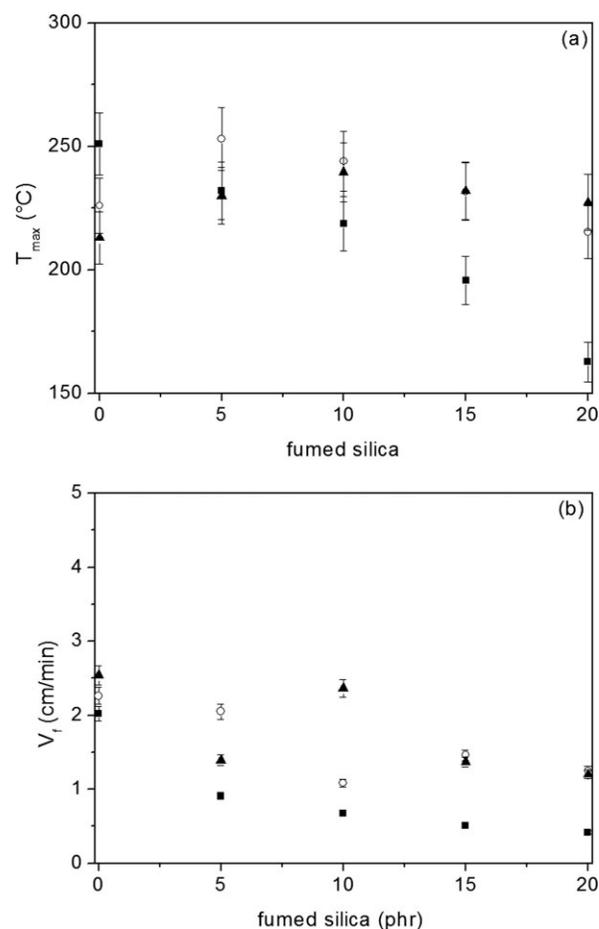
FIGURE 6 Front temperature (a) and front velocity (b) as functions of the amount of fumed silica for three different B-950 concentrations (■, 5 phr; ○, 10 phr; ▲, 15 phr).
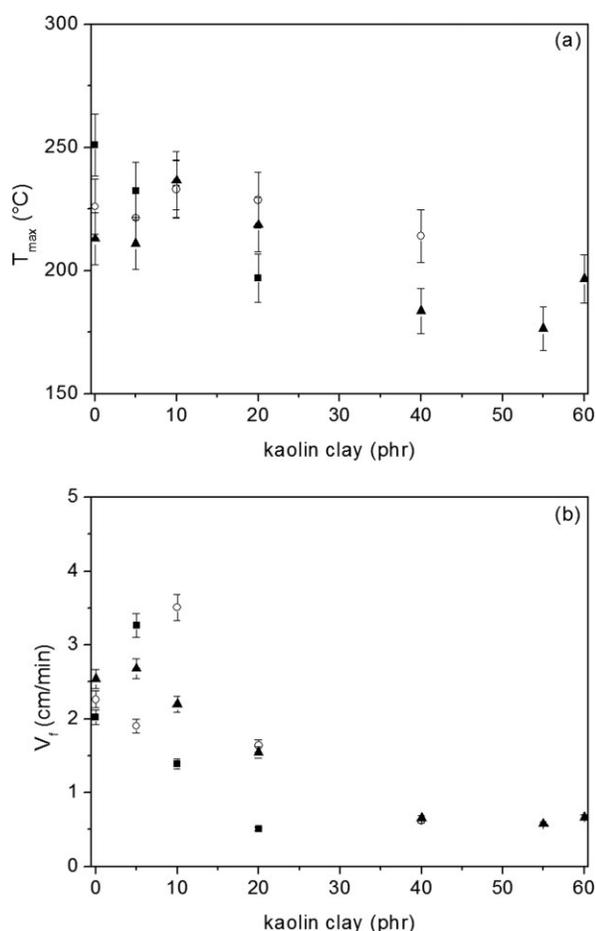
FIGURE 7 Front temperature (a) and front velocity (b) as functions of the amount of kaolin clay for three different B-950 concentrations (■, 5 phr; ○, 10 phr; ▲, 15 phr).

range of concentrations allowing for FP to self sustain was determined in the case of kaolin clay. As expected, it was found that, because of heat losses due to the presence of such an inert material, large amounts of filler could be used only if relatively high initiator concentrations were used.

By contrast, less fumed silica can be used because the material becomes too difficult to mold. However, the velocity and front temperature show the same trends as with kaolin clay. It is remarkable that using BF3-amine latent thermal initiators, it is possible to achieve the frontal curing of an epoxy resin while still maintaining a significant pot life.

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