

Frontal Cationic Curing of Epoxy Resins in the Presence of Defoaming or Expanding Compounds

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ABSTRACT: Thermal frontal polymerization was carried out with trimethylol propane triglycidyl ether using two different BF₃-amine complexes, B-950 and B-110 from Leepoxy, as initiators for cationic polymerization. The amounts of filler (kaolin or fumed silica), defoaming, or expansion agents were varied to study how the compositions affected the front velocity, expansion, and flexural modulus of the resulting epoxy resins. The polymer produced with B-950 initiator showed higher modulus than the polymers produced with B-110. Moreover, fumed silica created stronger materials than kaolin. The presence of BYK as a defoamer or an expansion agent such as the Expancel #80 was also able to affect significantly the mechanical properties. Differential scanning calorimetry studies indicated that the conversion was complete and that kaolin and silica increased the rate of reaction. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 40339.

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INTRODUCTION

Thermal frontal polymerization, which we will call simply “frontal polymerization” or FP, occurs when a monomer is converted to a polymer in a localized reaction zone that propagates through the coupling of thermal transport and the “Arrhenius” dependence of the reaction rate of an exothermic polymerization.^{1,2}

FP was first discovered by Chechilo et al.³ FP has many possible applications, including preparation of interpenetrating polymer networks,⁴ curing large composites,^{5–7} and material synthesis.^{8–10} Hu et al.¹¹ used free-radical FP to synthesize urethane-acrylate copolymers. Szalay et al.¹² polymerized an alternating styrene-maleic anhydride copolymer using free-radical FP. In 2004, Chen et al.¹³ synthesized polyurethane-nanosilica hybrid nanocomposites. Pojman and McCardle¹⁴ synthesized functionally gradient polymeric materials with short conversion times that were several centimeters in thickness. FP also may be used for the consolidation of the stone of historical monuments.¹⁵ Fiori et al.¹⁶ cured unsaturated polyester resin using FP and used hydroxyethyl acrylate in place of styrene to prepare unsaturated polyester resins. Nason et al.¹⁷ used a mixture of photoinitiators and thermal initiators for the

FP of acrylate and methacrylates. Hydrogels can be prepared by FP.^{18–24} FP can also be carried out in deep-eutectic mixtures.²⁵

Although most studies have focused on free-radical chemistry, other reaction mechanisms can be used including urethane formation²⁶ and ring-open metathesis polymerization.²⁷ FP has also been studied with epoxy-amine systems by Arutiunian and coworkers^{28,29} and Surkov et al.³⁰ modeled the frontal curing velocity. Chekanov et al.³¹ studied the frontal curing of epoxy resins with amines as did Mariani et al.^{32–34} Chen et al.³⁵ obtained epoxy resins/polyurethane networks. Pojman et al.^{4,36} studied binary FP in which the epoxy cured with amines and a BCl₃-amine complex.

This work extends our studies on the use of trimethylol propane triglycidyl ether (TMPTGE) with BF₃-amine complexes in the FP of epoxy resins.³⁷ Two BF₃-amine initiators, commercially named Leecure B-110 and B-950, were chosen because they have pot lives of 5 and 8 h, respectively, at 25°C, as reported by the manufacturer. Moreover, some fillers were also added; namely, kaolin (Al₂Si₂O₅(OH)₄, PolyGloss 90®),³⁸ fumed silica, a defoaming agent (BYK 070N) or an expansion agent (Expancel #80). The effects of the amount of the components on the front velocity, the front temperature, the expansion, and the mechanical properties are discussed.

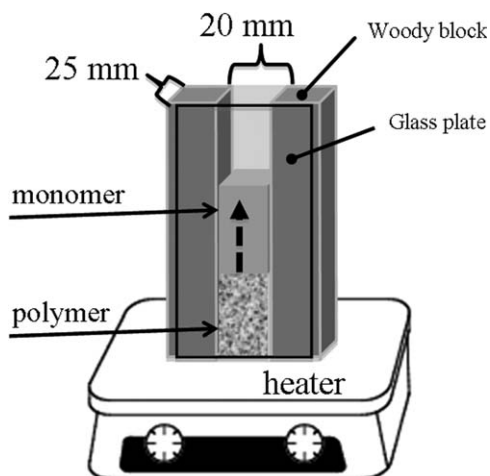


Figure 1. Illustration of the experimental setup and direction of front propagation.

EXPERIMENTAL

Materials

TMPTGE ($M_w = 302.36$, $d = 1.157 \text{ g cm}^{-3}$ at 25°C) was used as received from Aldrich. The BF_3 -amine initiators (Leecure B-110 and B-950) were obtained from Leepoxy (Fort Wayne, IN). B-110 and B-950 have a reported gel time at 80°C of 5 and of 11 min, respectively. Fumed silica (Aerosil 200, $\text{BET} = 200 \pm 25 \text{ m}^2 \text{ g}^{-1}$, size = 12 nm) was obtained from US Composites. The kaolin was PolyGloss 90® size = 400 nm, from Huber. BYK 070N (BYK USA; hereafter BYK) is a solution of 9% proprietary polymers in Xylene/Methoxypropyl acetate/Butyl acetate in ratios of 10/2/1. Expancel #80 (Expancel Inc.; hereafter Expancel) consists of thermoplastic microspheres from 18 to 24 microns in diameter, containing a hydrocarbon gas. The microspheres expand from 120 to 190°C . BYK and Expancel were also used as received.

Processing

Blend Preparation. In a typical run, a standardized wood mold ($200 \times 25 \times 20 \text{ mm}^3$) was loaded with TMPTGE (10 g), initiator [5 or 15 parts per hundred resin (phr)], BYK (0.12 phr), or Expancel (3 phr) and kaolin (20 or 60 phr) or fumed silica (5 or 20 phr). At larger contents of silica (more than 20 phr), the mixture became too viscous to be easily handled. The compounds were mixed at room temperature until a homogeneous mixture was obtained. The mixtures showed a pot life of more than 4 h regardless of the initiator or the filler used.

Mold Building. All surfaces in the mold were lined with masking tape and swabbed with mineral oil to facilitate removal of the product. The bottom of the mold was made entirely of masking tape in order for the thermal source to be applied at this point. The front of the mold consisted of a piece of glass, clamped into place (Figure 1).

Front Temperatures and Frontal Velocities Measurement. After the reactant mixture was in the mold, the sample was placed on a hot plate as shown in the Figure 1. Once a front was observed, the mold was removed from heat. The polymerization would propagate vertically. The high viscosity of the

resin allowed front propagation for most experiments without buoyancy-driven convection.³⁹

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 it was immersed at about 1.5 cm from the upper surface of the mixture. The front temperature 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, the front velocity was taken as 90% of the measured value. All experiments were performed in triplicate, and reported data are the averages.

Characterization Techniques

Infrared Analyses. A Fourier transform infrared spectroscope (FTIR; JASCO FT 480 spectrometer) was used for recording the FTIR spectra of the samples. The powders were ground into a dry KBr disk, and 32 scans at a resolution of 4 cm^{-1} were used to record the spectra.

Thermal Analyses. Differential Scanning Calorimetry (DSC) thermal characterization was performed by means of a Q100 Waters TA Instruments calorimeter, with TA Universal Analysis 2000 software. A heating-cool-heating cycle from -20 to 300°C , with a heating rate of 5°C min^{-1} and with a cooling rate $10^\circ\text{C min}^{-1}$, was carried out on dry samples. The first scan was performed to establish monomer conversion; the second one was to determine the glass transition temperatures (T_g), and a comparison between the two scans showed that conversions were always quantitative.

Mechanical Analyses. The 3-point flexural test mechanical analyses to provide the flexural moduli of composites were performed using a model 5582 Instron machine. The thickness of composite was 20 mm, and the length of the cantilever was 35 mm. The span of the composite was set up around 60–80 mm based on sample length. Considering both sample thickness and testing span, loading speed based on ASTM standard formula was calculated. The span and loading rate values were used for all sample groups. Thus, the measured bending strength and modulus should be valid and comparable among different groups.

RESULTS AND DISCUSSION

Polymerization of TMPTGE in the Presence of Defoaming or Expansion Agents with B-110 as Initiator

Thermal FP is a localized reaction that propagates through the reactants as a thermal wave where the propagating front can reach temperature up to 250 – 300°C depending on reactants.^{1,3} Under this reaction conditions, initiators like the BF_3 -amine complexes undergo a rapid thermal conversion to HBF_4 which is the initiating species (Figure 2).^{40,41} Thus, the reaction between TMPTGE and BF_3 -amine complexes such as B-110 or B-950 showed that the curing process consists of two main steps. The first step regards the complex formation reaction of

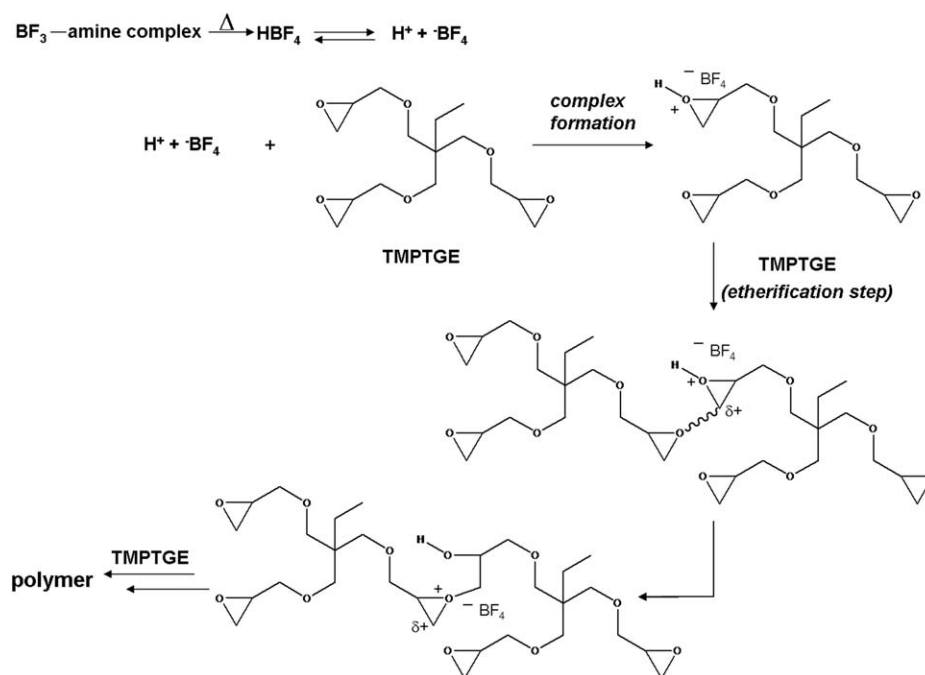


Figure 2. TMPTGE polymerization by complex formation and etherification reactions under FP conditions.

TMPTGE and the active species HBF_4 , and the second one is the etherification between the epoxy groups (Figure 2).^{40–45}

The maximum temperature (T_{max}) reached by the travelling front and its V_f are considered the two main parameters to be checked during an FP experiment. A typical temperature profile and front position vs. time data under FP conditions are plotted in Figure 3. Here, the polymer obtained in the presence of kaolin as filler (20 phr), BYK as defoaming agent and B-950 (15 phr) as initiator (sample FP12, Table I) shows the temperature profile [Figure 3(a)] in perfect accordance with a typical FP temperature behavior.³² Also, the frontal velocity of the sample FP12 was calculated by the front position as a function of the time as reported in Figure 3(b). The data are well fitted by a straight line, thus indicating that front propagates with a constant velocity, a feature typical of most FP systems. As can be seen, in this example as well as in all the other ones investigated in this work, all the FP experiments showed the similar FP profiles.

In Figure 4(a), all the front temperatures (T_{max}) with B-110 as the initiator and fumed silica as the filler are collected. The highest front temperature was achieved with the highest B-110 concentration. With 15 phr of initiator and 5 or 20 phr of filler,

the T_{max} ranged between 240 and 270°C. With 5 phr of B-110, the T_{max} ranged between 150 and 215°C.

Moreover, in all the systems considered, the T_{max} decreased as the amount of filler was increased because the inert filler absorbed heat. The same result was obtained using BYK (a defoaming agent) or Expancel (an expansion agent), which resulted in a T_{max} decrease in all the systems. The lowest T_{max} observed (150°C) was found with BYK and 20 phr of silica. It should be emphasized that the mixtures containing 20 phr of this filler and Expancel were not able to sustain FP regardless of the amounts of B-110 used.

Systems containing kaolin as filler (20 or 60 phr) were investigated, and the T_{max} values are reported in Figure 4(b). As observed with fumed silica [Figure 4(a)], the highest amount of B-110 resulted in the highest T_{max} regardless of amounts of other components. Thus, when 15 phr of B-110 were used, T_{max} ranged from 190 to 255°C but when the amount of B-110 was equal to 5 phr, T_{max} was lower, ranging from 160 to 185°C.

As far as the effect of the presence of kaolin, the highest T_{max} (255°C) was observed in the presence of 20 phr of filler and 15 phr

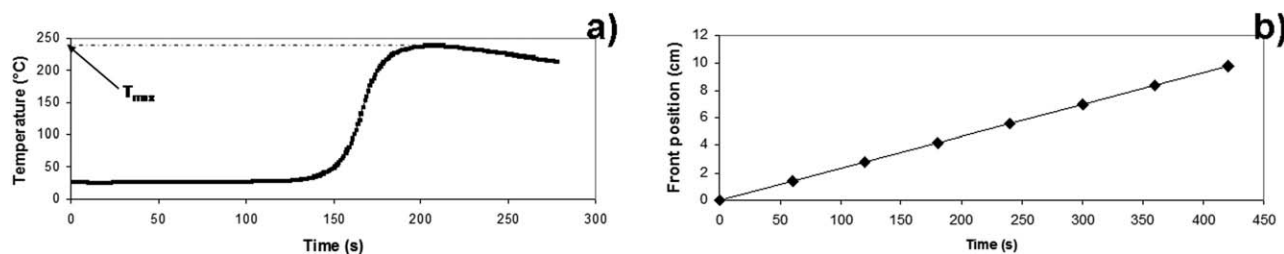


Figure 3. Sample FP12 and its FP parameters recorded: (a) Temperature profile and (b) Front position as a function of time in the presence of kaolin (20 phr), BYK, and B-950 (15 phr) as initiator.

Table I. Kinetic Parameters from DSC Measurements of TMPTGE-Fumed Silica or Kaolin Systems Cured in the Presence of B-110 or B-950 as Initiators

Sample name	Initiator	CI ^a (phr)	Filler	CF ^b (phr)	T _g (°C)	TA ^c (°C)	TB ^d (°C)	ΔH _{tot} (J g ⁻¹)	E _a (K J mol ⁻¹)	A (s ⁻¹)
FP1	B-110	5	Free		45.4	92		583	55	2.6 × 10 ⁶
FP2		10	Free		38.0	89		505	67	1.7 × 10 ⁸
FP3		15	Free		24.5	97		441	84	1.3 × 10 ¹¹
FP4		20	Free		-	85		505	70	8.3 × 10 ⁸
FP5		15	Fumed silica	20	44.5	99		510	72	6.7 × 10 ⁸
FP6		15	Kaolin	20	30.4	102		532	82	3.1 × 10 ¹⁰
FP7		15	Kaolin	60	21.6	109		520	65	1.2 × 10 ⁸
FP8	B-950	5	Free		55.6	84	120	603	57	1.1 × 10 ⁶
FP9		10	Free		45.8	85	120	530	60	6.2 × 10 ⁶
FP10		15	Free		17.8	92	128	435	56	2.6 × 10 ⁶
FP11		20	Free		-	84	114	494	59	4.8 × 10 ⁶
FP12		15	Fumed silica	20	30.7	96	129	513	51	5.5 × 10 ⁵
FP13		15	Kaolin	20	-	100	131	310	60	1.0 × 10 ⁷
FP14		15	Kaolin	60	13.4	100	134	544	57	5.6 × 10 ⁶

^aConcentration of initiator.

^bConcentration of filler.

^cTemperature of peak A.

^dTemperature of peak B.

of initiator, and the lowest (160°C) was found in the presence of 20 phr of filler, 5 phr of initiator and Expancel. Moreover, in the presence of 60 phr of kaolin, FP was observed only for the highest concentration of B-110 (i.e., 15 phr). This is probably due to the occurrence of vertical convective motions that made the front unstable. (Kaolin is not as an effective viscosifier as fumed silica.)

By making a comparison between the two mixtures having the same fumed silica or kaolin concentration (20 phr), it was found that the presence of kaolin resulted in higher T_{max} values [Figure 4(a,b), respectively].

The front velocities of the systems described above are reported in Figure 5. As expected, with fumed silica [Figure 5(a)], all three sets of experiments (without any additive, or in the presence of BYK or Expancel) show that the front velocity increased as the amount of

initiator was increased and decreased as the amount of filler increased. While 15 phr of B-110 led to front velocities between 2.4 cm min⁻¹ (5 phr of fumed silica, BYK) and 1.1 cm min⁻¹ (20 phr of fumed silica, BYK), when 5 phr of B-110 were used, front velocities were lower and ranged between 0.6 cm min⁻¹ (5 phr of fumed silica, BYK) down and 0.20 cm min⁻¹ (20 phr of fumed silica, BYK). The higher initiator concentrations increased the reaction rate, which decreased the time for heat loss. Moreover, larger concentrations of filler resulted in more heat absorption, thus lowering both T_{max} and the reaction rate. For the same initiator concentration, the presence of BYK increases the front velocity. We propose that BYK reduces void formation and thus increases the effective thermal diffusivity of the medium. However, adding Expancel the polymerization produced the lowest velocities. In particular, FP would not occur with Expancel-containing mixtures

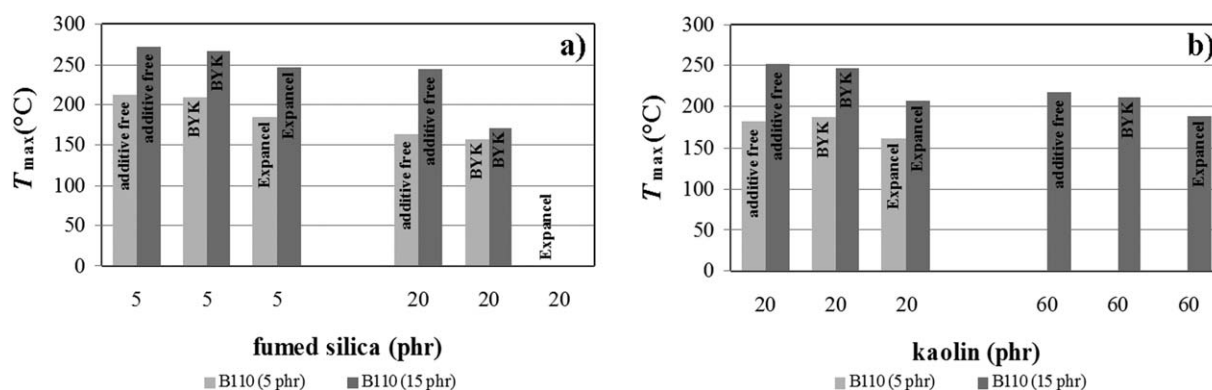


Figure 4. The front temperatures for the experiments with: (a) fumed silica and (b) kaolin as fillers in the presence of BYK or Expancel, initiated by 5 (light gray bars) or 15 phr of B-110 (dark gray bars).

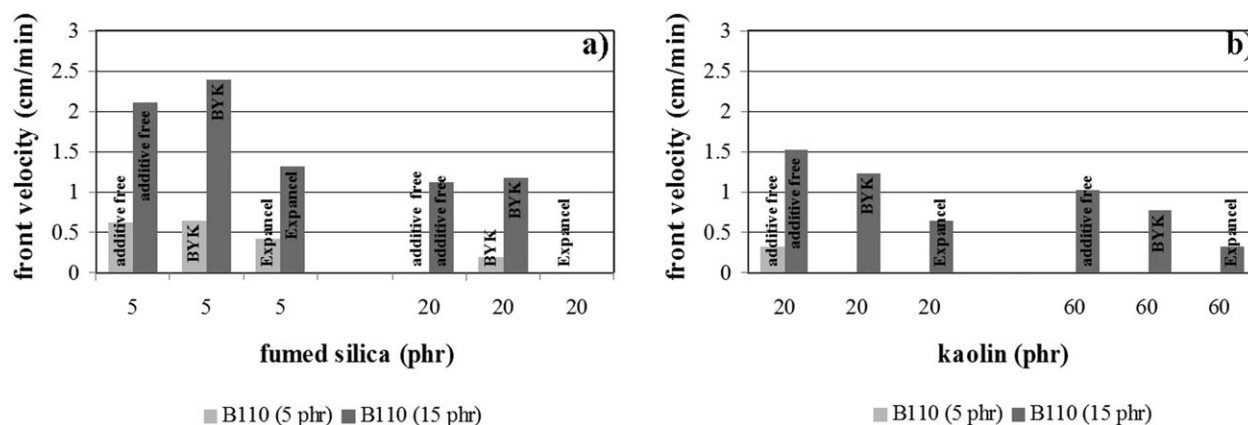


Figure 5. Front velocity of the systems with: (a) fumed silica and (b) kaolin as fillers in the presence of BYK or Expancel, initiated by 5 phr (light gray bars) or 15 phr of B-110 (dark gray bars).

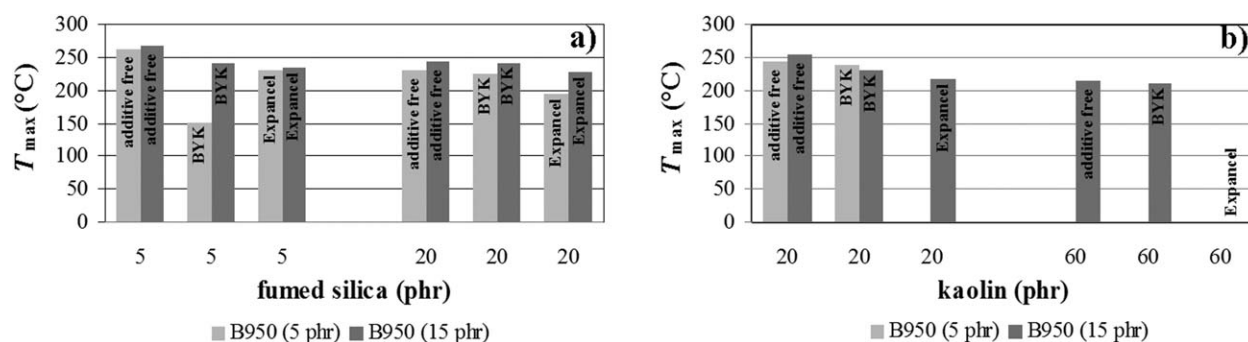


Figure 6. T_{max} of the systems with: (a) fumed silica and (b) kaolin as fillers in the presence of BYK or Expancel, initiated by 5 phr (light gray bars) or 15 phr of B-950 (dark gray bars).

when the amount of fumed silica was higher than 5 phr. We propose the expanded regions formed by the Expancel reduce the thermal diffusivity and thus reduce the front velocity.

In Figure 5(b), the front velocities of the mixtures in which kaolin was substituted for fumed silica are shown. Again, the front velocity increased with the amount of initiator and decreased with increasing of filler loading. Front velocities with kaolin were higher than those found when same amount of fumed silica was used. We propose that this is due to some

interaction of the B-110 initiator with either silica and/or kaolin that affects its reactivity.

Polymerization of TMPTGE in the Presence of Defoaming or Expansion agents with B-950

In a second set of experiments, blends with various compositions made of fumed silica, kaolin and in the presence of BYK or Expancel were investigated by using 5 or 15 phr of B-950 as initiators. The corresponding T_{max} and V_f values are reported in Figures 6 and 7.

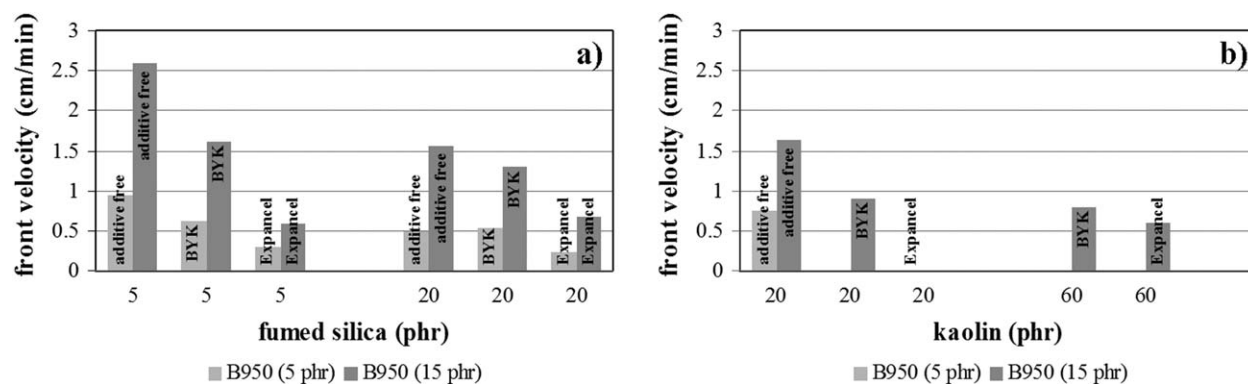


Figure 7. Front velocity of the systems with: (a) fumed silica and (b) kaolin as fillers in the presence of BYK or Expancel, initiated by 5 phr (light gray bars) or 15 phr of B-950 (dark gray bars).

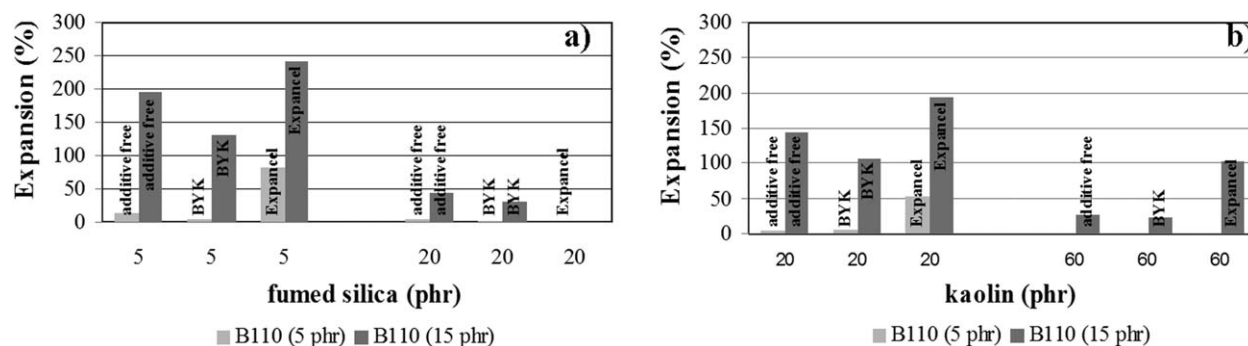


Figure 8. Volume change of systems with: (a) fumed silica and (b) kaolin in the presence of Expancel (3 phr) or BYK (0.5% mass). The dark gray bars indicate the use of 15 phr of B-110, while light gray ones indicate a B-110 concentration of 5 phr.

For systems containing 5 or 20 phr of fumed silica [Figure 6(a)], the front temperature increased as the amount of initiator was increased and decreased as the filler was increased. Thus, by using 15 phr of B-950, T_{\max} ranged between 230°C (20 phr of fumed silica, Expancel) and 240°C (5 phr of fumed silica and BYK). However, when 5 phr of B-950 were used, T_{\max} varied between 150°C (5 phr of fumed silica and BYK) and 190°C (20 phr of fumed silica, Expancel).

It can be observed, from Figure 6(a), that T_{\max} decreased in the presence of BYK or Expancel. In Figure 6(b), T_{\max} values of the experiments containing 20 or 60 phr of kaolin are reported. Only compositions with 15 phr of B-950 were able to support FP throughout the range of filler investigated.

For the systems with B-950, in the presence of fumed silica [Figure 7(a)], regardless of the additive added, V_f increased as the amount of initiator increased and decreased as the amount of filler increased. For 15 phr of B-950, the highest V_f (2.6 cm min⁻¹) was reached by mixing 5 phr of filler without any additive; the lowest velocity was observed in the presence of Expancel with 5 phr of filler. The V_f measured in the experiments carried out by using 5 phr of B-950 ranged between 0.90 cm min⁻¹ (5 phr fumed silica, additive free) and 0.25 cm min⁻¹ (20 phr fumed silica with Expancel). For the same amount of filler, systems with kaolin and silica had comparable front velocities if a front propagated. We propose that the B-950 interacts differently with the fillers than B-110.

The V_f recorded for the systems with kaolin as filler and B-950 as initiator are reported in Figure 7(b). The front velocity

increased as the amount of initiator was increased and decreased as the amount of filler was increased. Moreover, it was also affected by the presence of the defoaming or bubble-generating additives. In the presence of 15 phr of B-950, the V_f varied between 0.6 cm min⁻¹ (60 phr of kaolin and BYK) and 1.6 cm min⁻¹ (20 phr of kaolin and no additive).

It is worth noting that while 5 phr of B-110 in the presence of Expancel and 20 phr of fumed silica [Figure 5(a)] was not able to produce a self-sustaining front, 5 phr of B-950 could sustain a polymerization front [Figure 7(a)]. FPs carried out with B-950 propagated faster and with higher T_{\max} values than those performed with B-110.

System Expansion and Property Investigations

Expansion Studies. The effects of an expansion agent (Expancel) and a defoaming agent on the product volume of the obtained materials were studied in the presence of either fumed silica or kaolin as a function of B-110 concentration. By comparing the highest initiator concentration systems (15 phr) with the lowest ones (5 phr) prepared in the presence of 5 or 20 phr of fumed silica, we can see that increasing the initiator concentration led to larger volume expansion [Figure 8(a)]. Obviously, the volume expansion was much larger when Expancel was used instead of BYK because Expancel consists of microspheres that expand when heated. Expancel generated a significant volume increase (up to 240%) in the presence of 5 phr of fumed silica and 15 phr of B-110.

When kaolin was used instead of fumed silica in the system discussed above (by keeping the additive concentration at 20 phr),

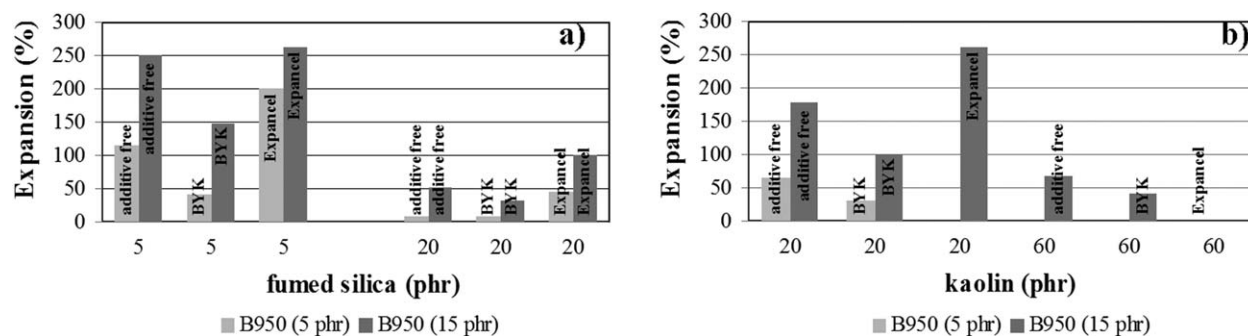


Figure 9. Expansion of systems with: (a) fumed silica and (b) kaolin in the presence of Expancel (3 phr) or BYK (0.5% mass). The dark gray bars indicate high initiator concentration (15 phr) and the light gray bars indicate low initiator (5 phr) concentrations of B-950.

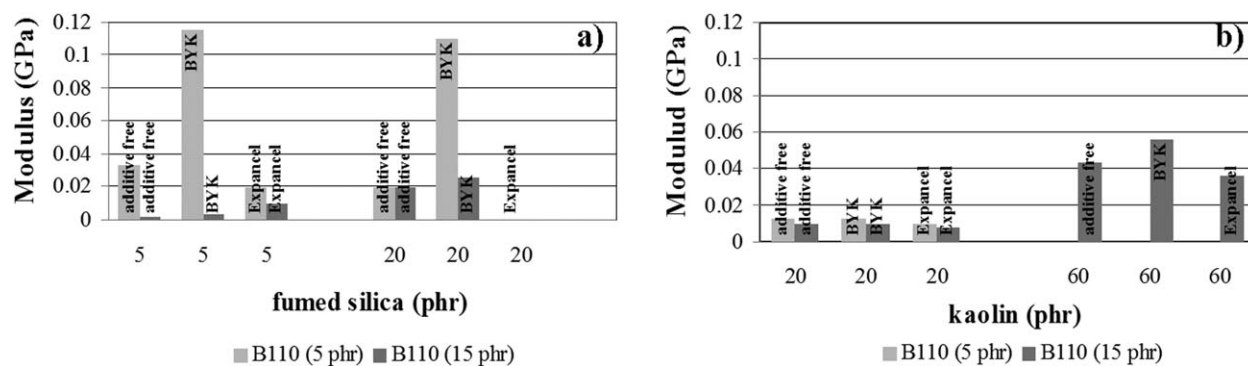


Figure 10. Moduli for systems with: (a) fumed silica and (b) kaolin in the presence of Expancel (3 phr) or BYK (0.5% mass). The dark bars indicate high initiator concentration (15 phr) and the light gray bars indicate low initiator (5 phr) concentration of B-110.

a larger volume increase was found [Figure 8(b)]. We propose that the fumed silica interacts more strongly with the resin than kaolin and suppress expansion. As expected, the increase of kaolin loading to 60 phr resulted in a decrease in volume expansion when compared with the systems containing less foaming agent. An analogous study was carried out with B-950 as initiator. From a qualitative point of view, the results obtained are similar to those for B-110 (Figure 9).

Mechanical Properties. The flexural modulus of the composite materials was measured, and the data are displayed in Figures 10 and 11. It was found that the larger the amount of additive (kaolin or fumed silica), the larger the modulus. By contrast, the modulus decreased as the initiator concentration was increased.

The modulus was lower with Expancel instead of BYK. Moreover, the larger was the amount of foaming agent the lower was the modulus. The systems cured in the presence of fumed silica [Figure 10(a)] and 15 phr of B-110 showed a modulus ranging between 0.025 GPa (20 phr of fumed silica and BYK) and 0.01 GPa (5 phr of fumed silica and additive free). In contrast, when 5 phr of B-110 were used, the modulus ranged between 0.12 GPa (5 phr of fumed silica and BYK) and 0.02 GPa (5 phr of fumed silica and Expancel). In the presence of kaolin [Figure 10(b)], no significant differences were observed between 15 phr of B-110 and B-950.

The moduli for the system with B-950 as initiator and with fumed silica or kaolin as fillers are plotted in Figure 11. Again,

the modulus increased as the amounts of initiator decreased and increased as the filler increased. In the presence of fumed silica [Figure 11(a)], large modulus differences were obtained, depending on the amounts of initiator used. With 15 phr of B-950, the modulus was almost constant ranging between 0.01 GPa (5 phr of fumed silica and BYK) and 0.03 GPa (20 phr of fumed silica and Expancel). Using 5 phr of initiator, it reached higher values ranging between 0.47 GPa (5 phr of fumed silica and BYK) and 0.25 GPa (5 phr of fumed silica and Expancel).

By using kaolin [Figure 11(b)], with 15 phr of initiator the modulus ranged between 0.01 GPa (5 phr of filler and regardless of the additive) and 0.55 GPa (60 phr of filler and BYK). Due to the difficulty of obtaining FP in the systems made of 5 phr of initiator and 60 phr of kaolin as already previously described, only a few moduli could be measured. Thus, only two points are reported in Figure 11(b) for this last composition: 0.04 GPa (20 phr of filler and additive free) and 0.07 GPa (20 phr of filler and BYK).

As reported in Figures 10 and 11, although the inorganic fillers are chemically inert,⁴⁶ the type and particle size of the filler affects the mechanical properties. We propose that silica produced composites with higher stiffness than kaolin because of the silica's higher surface area and ability to hydrogen bond with the matrix. The presence of BYK as a defoamer increased the modulus because it reduced bubble formation and thus the polymer flexibility decreased. However, the presence of Expancel decreased the modulus (decreasing the stiffness) because it

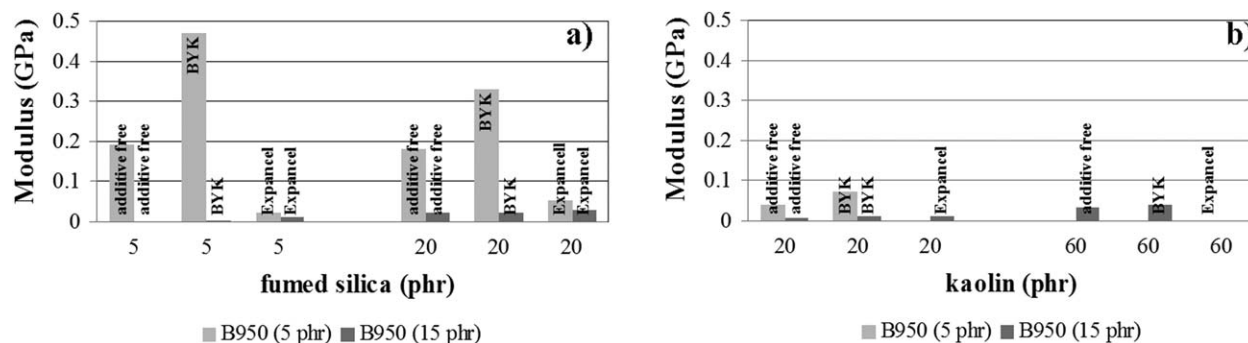


Figure 11. Moduli measured on systems with (a) fumed silica and (b) kaolin with Expancel (3 phr) or BYK (0.5% mass). The dark gray bars indicate high initiator concentration (15 phr), and the light gray bars indicate low initiator (5 phr) concentrations of B-950.

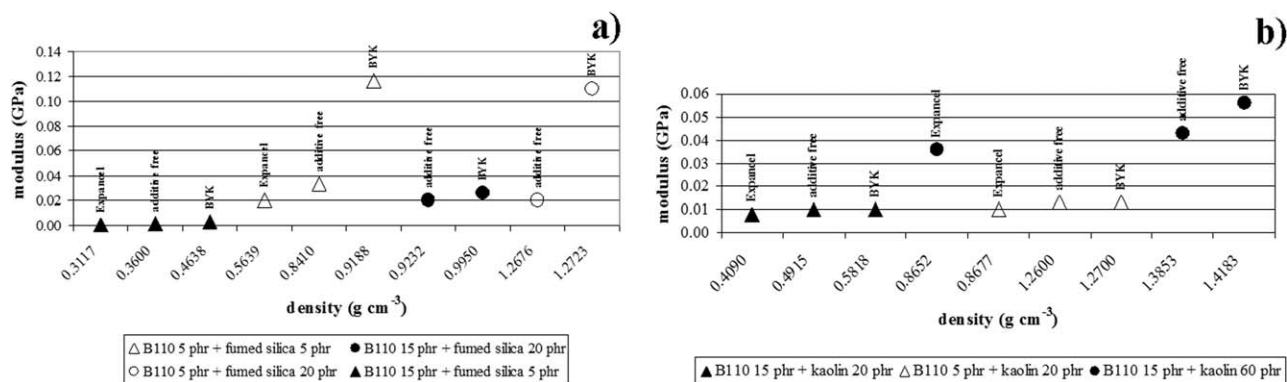


Figure 12. Moduli and density measured on systems composed by B110 as initiator, Expancel (3 phr), or BYK (0.5% mass) and in the presence of (a) fumed silica and (b) kaolin.

generated numerous bubbles that reduced the stiffness of the material. The results till now reported, showed also that the initiator affects on the mechanical properties of the final polymer. The presence of B-110 as initiator (Figure 10) decreased the stiffness compared with the polymers prepared with B-950 (Figure 11).

The moduli are also a function of the porosity of the cured epoxy but porosity alone cannot explain the variations in moduli. The densities of the polymers obtained with B110 and B950 were measured and plotted in Figures 12 and 13, respectively.

First, polymer systems obtained by B110 and containing fumed silica are considered [Figure 12(a)]. In this kind of system, density increased as the filler amounts increased. The density in systems containing 5 phr of fumed silica is ranging between 0.31 and 0.92 g cm⁻³, while in the systems with 20 phr of filler is ranging between 0.92 and 1.3 g cm⁻³. Also, in both systems (5 and 20 phr of filler), 5 phr of B110 are able to get polymers with higher density than polymers obtained by 15 phr of initiator. Moreover, Expancel and BYK are able to affect the density (and modulus) of the polymers. The presence of BYK increased the modulus and density more than Expancel. That is because by BYK, bubbles formation was decreased and the density increased, thus polymers so obtained are more stiff.

The highest moduli 1.5×10^{-1} and 1.7×10^{-1} GPa are observed in polymers obtained in the presence of 5 phr of

B110, BYK, and containing 5 and 20 phr of fumed silica respectively. However, greater flexibility is obtained by high concentrations of catalyst and low concentrations of filler. We propose that this is due to the formation of voids.

Polymers obtained by B110 and containing kaolin are considered in Figure 12(b). Density increased in the presence of BYK and as the filler amount increased. Again, higher density is obtained in the presence of low amounts of B110 such as 5 phr. However, the highest density (1.4 g cm⁻³) is observed in polymers containing 60 phr of kaolin, 15 phr of B110 and in the presence of BYK as defoaming agent. The amount of catalyst do not have a strong effect on modulus when 20 phr of kaolin is used; moduli are around 1×10^{-2} GPa. The highest modulus (5.5×10^{-2} GPa) is obtained by 15 phr of B110 and 60 phr of kaolin but in the presence of BYK.

Comparing the filler used, 20 phr of silica [Figure 12(a)] generated polymers with higher density and modulus than 20 phr of kaolin ones [Figure 12(b)]. That could be due to the hydrogen bonding of the silica to the polymer.

Density and moduli of the polymers obtained by B950 in the presence of fumed silica and kaolin are reported on Figure 13. First, systems containing fumed silica as fillers are considered [Figure 13(a)]. As expected, density increased as fumed silica amounts increased, starting from 0.29 (filler 5 phr, B950 15 phr, and Expancel) to 1.3 g cm⁻³ (filler 20 phr, B950 5 phr, and

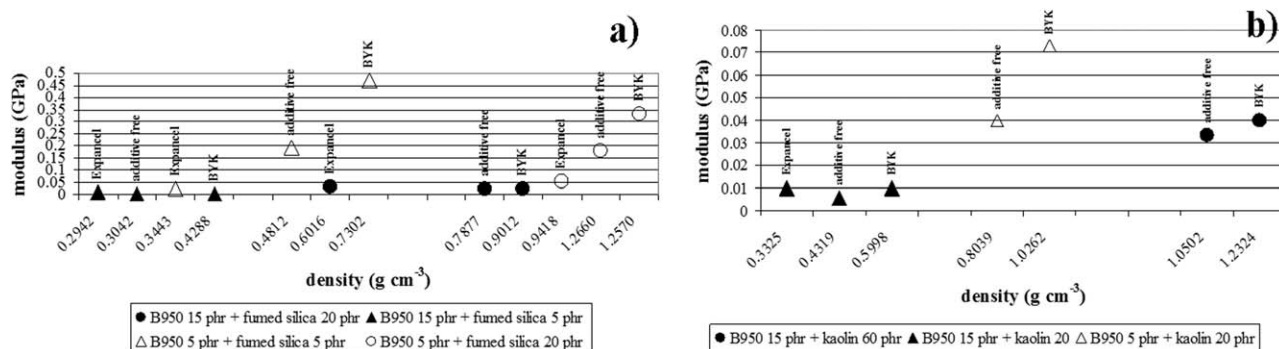


Figure 13. Moduli and density measured on systems composed by B950 as initiator, Expancel (3 phr), or BYK (0.5% mass) and in the presence of (a) fumed silica and (b) kaolin.

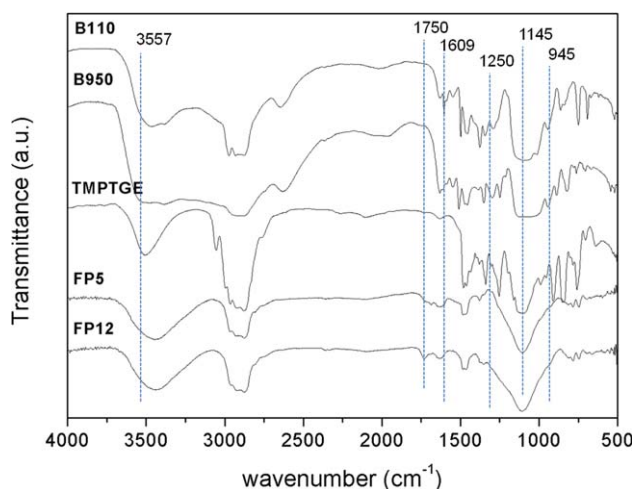


Figure 14. FTIR analysis on samples cured by B-110 (FP5) or B-950 (FP12), and in the presence of 20 phr of fumed silica, compared with the starting monomer and initiators. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

BYK). Moduli values suggest the additives like Expancel and BYK affect strongly the systems in the presence of 5 phr of B950. BYK is able to increase the modulus up to 0.47 GPa in the presence of 5 phr of B950 and 5 phr of fumed silica. However, Expancel is able to reduce modulus to 0.30 GPa (higher flexibility) when 15 phr of B950 and 5 phr of fumed silica are used.

The polymer systems carried out in the presence of B950 and kaolin are considered in Figure 13(b). Again, the highest density 1.2 g cm^{-3} , is obtained in the presence of the highest amounts of filler (60 phr of kaolin) and 15 phr of B950. However, in this last case, the modulus decreased. Low amounts of catalyst (5 phr) and filler (20 phr) showed the highest modulus reaching $7.3 \times 10^{-2} \text{ GPa}$ when BYK is used.

As already observed in the systems made by B110 (Figure 12), also in the presence of B950, systems with 20 phr of silica [Figure 13(a)] generated polymers with higher density and modulus than 20 phr of kaolin ones [Figure 13(b)]. Regarding the catalyst used, B950 polymer systems showed higher modulus and lower density than samples prepared with B110.

Spectral and Kinetic Properties. Infrared investigations. Typical FTIR spectra of the polymerizing components (i.e., B-110, B-950 and the epoxy monomer) are shown in Figure 14. The main peaks are at: 3557 cm^{-1} (NH stretching), 3000 cm^{-1} (CH stretching), 1609 cm^{-1} (NH bending), 945 and 1145 cm^{-1} (BF symmetric and asymmetric stretching of BF_3 , which is probably one of the components of B-110 and B-950), 1070 cm^{-1} (BF_4^-).^{40,41}

In addition, the two spectra of the samples FP5 and FP12 containing 15 phr of silica and synthesized in the presence of B-110 and B-950 as initiator respectively (Table I) are also displayed for comparison on Figure 14. The peaks at 3000 cm^{-1} of the composite samples are enlarged compared with the corresponding ones for the starting materials; however, the CH stretch is still clearly visible, whereas the NH peaks at 1609 cm^{-1} are not.

The peaks that were present between 1200 and 1750 cm^{-1} in the initiator spectra have either disappeared or are greatly diminished in size. On this basis, and considering what is reported in the literature,⁴¹ we propose that the BF_3 -amine complexes (B-110 and B-950) convert to HBF_4 at the high temperatures reached during FP.^{40,41}

Thermal analyses. Blends containing fumed silica or kaolin as filler with B-110 or B-950 as initiator, were analyzed by DSC to obtain the kinetic parameters of the curing reaction, following the method proposed by Barrett.⁴² As also reported by Ghaemy and Khandani,⁴¹ the extent of reaction, named as a , is given by eq. (1) where H is the heat developed up to a certain temperature (partial area under a DSC peak) and ΔH is proportional to the total heat of reaction (the total area under the DSC traces).

$$a = H / \Delta H \quad (1)$$

Since, the thermal event is the polymerization, the reaction rate da/dt is directly proportional to the dH/dt as reported by eq. (2):

$$da/dt = 1/\Delta H \times dH/dt \quad (2)$$

which can be written in differential form as eq. (3):

$$da/dt = kf(a) \quad (3)$$

Thus, by some mathematical steps and taking into consideration the Arrhenius equation, the eq. (3) furnishes the equation for the derivative analysis of the dynamic data [eq. (4)].⁴¹ Computationally it is possible to calculate the expression $\ln[(da/dt)/f(a)]$ (R is the gas constant, T is the temperature) for each conversion point, yielding the values of activation energy (E_a) and the frequency factor (A).

$$\ln[(da/dt)/f(a)] = \ln k = \ln A - E_a/RT \quad (4)$$

All the kinetic results carried out in this work are reported in Table I. It was found that when no filler was used, ΔH decreased with increasing initiator concentration, which is to be expected because the initiator itself does not contribute to heat production. However, we cannot explain why the enthalpies for both initiators at 20 phr is higher than at 15 phr.

By comparing the DSC thermograms of the samples obtained using B-110 with those initiated by B-950, distinct thermal behavior is clearly visible in all samples (Figure 15). All

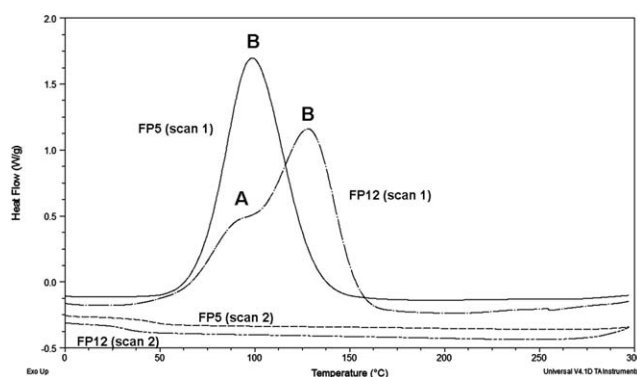


Figure 15. DSC first and second scans of samples FP5 and FP12 containing 20 phr of fumed silica and 15 phr of B-110 or B-950, respectively.

thermograms of the samples obtained by using B-950 exhibited a shoulder (point A), while all the others do not.

The presence of the shoulder is in agreement with literature reports and can be attributed to the formation of a complex between HBF_4 and the monomer⁴¹ (Figure 2). However, such a complex does not seem to form when B-110 is used. Since both these initiators are commercial and their actual compositions are not known, it is not possible to confirm this hypothesis.

The second (larger) peak (Figure 15, peak B), which is the only one present in all samples independent of the initiator utilized, was due to the polymerization by ether formation. This exothermic peak is that used for the kinetic studies.^{41,42} By comparing the thermograms of the samples obtained using B-110 and B-950, it can be seen that the former reaches a maximum at a lower temperature, thus indicating that this initiator is more reactive than B-950 (Figure 15).⁴¹

It is also noteworthy that the filler largely affects the T_g and the frequency factor as well (Table I). The glass transition temperatures of the samples with no filler FP1-3 (B110 as initiator) are higher if compared with the samples FP5-7 (with filler). The same behavior can be observed if B950 is used. Samples without filler FP8-10 show higher T_g than FP12-14 (with filler). We do not have a explanation for the decrease in glass transition temperature caused by the filler. The higher B-110 initiator activity is also confirmed by the frequency factor (A), which is higher than that of B-950 (Table I).

With B-110 the A value decreases from $1.3 \times 10^{11} \text{ s}^{-1}$ when no filler is present down to $3.1 \times 10^{10} \text{ s}^{-1}$ (in the presence of kaolin, sample FP6) and to $6.7 \times 10^8 \text{ s}^{-1}$ (in the presence of silica, sample FP5). When B-950 is used, a similar trend is found but the difference among filler-free and filler-containing samples is not as large. These results suggest some catalytic activity of the fillers.

CONCLUSION

The FPs of TMPTGE using two latent cationic initiators were studied. The effects of initiator concentration and filler type and loading on the front velocity, front temperature, and flexural modulus were determined. The polymer catalyzed by B-950 initiator showed higher modulus than the polymers catalyzed by B-110. Moreover, fumed silica as filler produced stiffer materials than if kaolin was used as the filler. The presence of BYK as a defoamer or an expansion agent such as the Expancel #80 was also able to change dramatically the mechanical properties. The reduction in voids by BYK was able to increase the stiffness five times over that obtained with Expancel.

FITR studies suggested that the initiators form a complex between HBF_4 and the monomer. DSC showed that the reaction rate was increased by fumed silica and kaolin and that the reaction enthalpy generally decreased with high amounts of initiator.

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