

Suspension polymerization casting of lead zirconate titanate, Part II: acrylate system

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Abstract Suspension polymerization casting of lead zirconate titanate (PZT) filled acrylate-based system was investigated using 51 vol% suspension of PZT in an ethoxyethoxy ethyl acrylate-based system. The polymerization process was characterized with chemorheology and differential scanning calorimetry. PZT powder accelerates the process, decreasing the activation energy for polymerization from 132 ± 6 kJ/mol to 98 ± 20 kJ/mol. The influence of monomer ratio, initiator amount, catalyst, and solvent are presented.

Introduction

The technique of solidifying a ceramic suspension by polymerizing the medium (or gel casting) has been widely reported [1–6]. A concentrated suspension of ceramic powders, dispersed in a monomer solution are introduced into mold where the monomers are polymerized in situ. This produces a solid object consisting of ceramic powders entrapped in a polymer gel network. In part I of this series [7], we reported on suspension polymerization casting (SPC) of lead zirconate titanate (PZT) ceramics using an acrylamide hydrogel-based system. This paper concerns a

non-aqueous acrylate system, which produces a stronger, more rigid object upon molding, since it contains a large fraction of cured polymer as binder. Removing that polymer before sintering, however, requires a slow and difficult binder burnout process. Acrylamide hydrogel systems produces a softer object upon molding, since the hydrogel binder is not rigid until after a drying. This is disadvantageous for large thin-walled objects, which require handling the soft wet state. However, while dried acrylamide hydrogel objects have no burnout problem, the drying of hydrogels can cause cracking in gelcast bodies. To minimize severe warpage and cracking, drying is done slowly at very high relative humidity. Although the dried green body is very strong [6], the as-cured wet body is soft. As a result, it is difficult to keep the green body intact during demolding process. In order to use an acrylamide system to build complex shapes with high aspect ratios and large surface areas, additional aids are needed, such as using a fugitive wax mold [5], and machining dried green body [8]. Thus there are applications where the acrylate SPC process is preferred. Acrylate SPC can either use pure monomers, or a solution of monomer with a non-volatile solvent, such as decalin or dibasic esters. With a solvent present, the monomer polymerizes to a solvent-swollen gel. This was, in fact, the gel-casting process that was first reported by Janney [1] and Venkataswamy et al. [2].

The polymerization reaction is the key step in the process. The kinetics and mechanisms of the polymerization of ceramic powder-filled monomer solutions have been reported for photopolymerization [9, 10] for a variety of powders and monomers based on hexane diol-diacrylate (HDDA). The chemistry of the photopolymerization process is similar, although the optical properties of the powder play a decisive role [11, 12] that is not a factor with thermal polymerization. Chu [13] reported on the thermal

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polymerization for a monomer solution of propoxylated neopentoglycol diacrylate (PNPGDA) and isobornyl acrylate (IBA) with Al_2O_3 and hydroxyapatite powder. Thermal analysis showed that the ceramic powder affects the polymerization process. The current study extends previous research in SPC process, with 2-(2-ethoxyethoxy) ethyl acrylate (EOEOEA) and propoxylated neopentyl glycol diacrylate (PNPGDA) as the monomer system.

Polymerization mechanism

A ratio of monofunctional and difunctional monomers in the monomer mixture plays an important role. Larger amounts of difunctional monomer is expected to increase the network strength by crosslinking, but the effect is not simple because intermolecular crosslinking competes with intramolecular cyclization. For the methyl methacrylate/ethylene glycol dimethacrylate (MMA/EGDM) system, Okay et al. [14] reported an increase in the dimethacrylate increase intramolecular links, but Tobita and Hamielec [15] reported that as much as 80% of pendant double bonds cyclize rather than crosslink.

A unique feature of SPC is polymerization in the presence of ceramic powder. There is relevant literature for the use of similar powders added in smaller quantities as fillers [16–18]. The polymerization process is often accelerated in the presence of these fillers, especially carbon black [17]. Filler also can have an impact on heat transfer during polymerization, which in turn will change the curing rate [19]. Chu et al. [13] showed that acrylate polymerization was faster in the presence of Al_2O_3 or hydroxyapatite. Initiator also plays an important role in polymerization, with an accelerated polymerization with an increase in initiator concentration. However, the molecular mass of the end product is determined by the ratio of molar concentrations of monomer and initiator, so increases in initiator concentration may lead to a weaker network [20]. Temperature has a great influence over all of the steps in the polymerization process, such as initiator decomposition, radical transport and termination.

Experimental procedures

Processing

Table 1 lists all of the materials involved in the current study, with materials composition, function, and sources. The PZT powder median particle size (D_{50}) 1.1 μm , a specific surface area of this powder of 0.75 m^2/g , and density of 7.7 g/cm^3 . The suspension medium was a mixture of difunctional monomer propoxylated neopentyl

glycol diacrylate (PNPDGA), monofunctional monomer is 2-(2-ethoxyethoxy) ethyl acrylate esters (EOEOEA). Note that the acrylates contained about 400 ppm hydroquinone monomethyl ether polymerization inhibitor. Decahydronaphthalene (decalin), was used as a non-reactive diluent. Suspensions were prepared using this mixture and 51 volume percent PZT powder, with 1 wt% Emcol CC-55 (Witco Corp, Dublin, OH) as dispersant, and ball milled with zirconia media for 24 hours. The suspension was deaired in a rotary vacuum system until no air bubbles were observed (usually it took about three minutes). Benzoyl peroxide (BPO, Aldrich, Milwaukee, WI) to initialize the free-radical polymerization. To have a homogeneous distribution, BPO was dissolved in acetone (0.1 g/ml), and then added into the deaired suspension. The suspension with initiator added was further deaired in the rotary evaporator, which removed most of the acetone. The BPO amount was set as 0.15 wt% of slurry, which is about 1.5 wt% of powder-free monomer solution. The typical compositions for monomer solution and PZT slurry are shown in Tables 2 and 3. Figure 1 shows the chemical structures for the monomers, initiator, and catalyst.

For some cases, the polymerization temperature was reduced with the use of *c*N,N-Dimethyl-*p*-Toluidine (DMPT) to catalyze the decomposition of the BPO. Adding DMPT directly caused curing to begin before mixing was complete. To avoid this we prepared one PZT suspension with BPO but no DMPT, the other with DMPT, but no BPO. The two suspensions were deaired, then cooled to 0 °C, where they could be mixed without reaction. The amount of initiator and catalyst used could vary in a wide region, primary depends on the operation temperature and time required by the process. In our case, 0.1 wt% of initiator and 0.025 wt% catalyst were used to get about 10 min operation time before polymerization started. The mold is filled with the fluid suspension and cured at 40–90 °C, depending on the amount of initiator and/or the amount of catalyst. After polymerization, the ceramic body was removed from the mold and slowly heated (8–10 °C/h) to 700 °C to burn out the polyacrylate. After burnout, sintering was carried out at 1275 °C for 4 h, with a heating rate 2.5 °C/min.

Characterization of suspension polymerization

The rheological properties of the suspension before polymerization were characterized in steady shear by a concentric cylinder rheometer (Bohlin Rheolgi CS-50, Cranbury, NJ). Before the measurement, the sample was agitated to reach equilibrium. The data was taken from the increasing shear rate curve. The polymerization process was monitored by oscillatory measurement, using a parallel plate system in the same rheometer, with a 0.5 mm gap

Table 1 Materials used in suspension polymerization casting

Materials	Function	Compositions	Source
Lead Zirconate Titanate (PZT)	Ceramic powder	Pb(Zr _{0.52} Ti _{0.48})O ₃	American Piezo, Mackeyville, PA
2-(2-Ethoxyethoxy) Ethy Acrylate (EOEOEA)	Monofunctional monomer	see (1)	Sartomer, West Chester, PA
Propoxylated Neopentyl Glycol Diacrylate (PNPGDA)	Difunctional monomer	see (2)	Sartomer, West Chester, PA
Decahydronaphthalene (decalin)	Diluent Solvent	see (3)	Avocado, heysham, Lancs, UK
Emcol CC-55	Dispersant	Not available	Witco, Dublin, OH
Benzoyl Peroxide (BPO)	Free radical initiator	see (4)	Aldrich, Milwaukee, WI
N, N-Dimethyl-p-Toluidine (DMPT)	Catalyst to BPO decomposition	see (5)	Aldrich, Milwaukee, WI

Table 2 Typical composition for premixture with monomer ratio 25

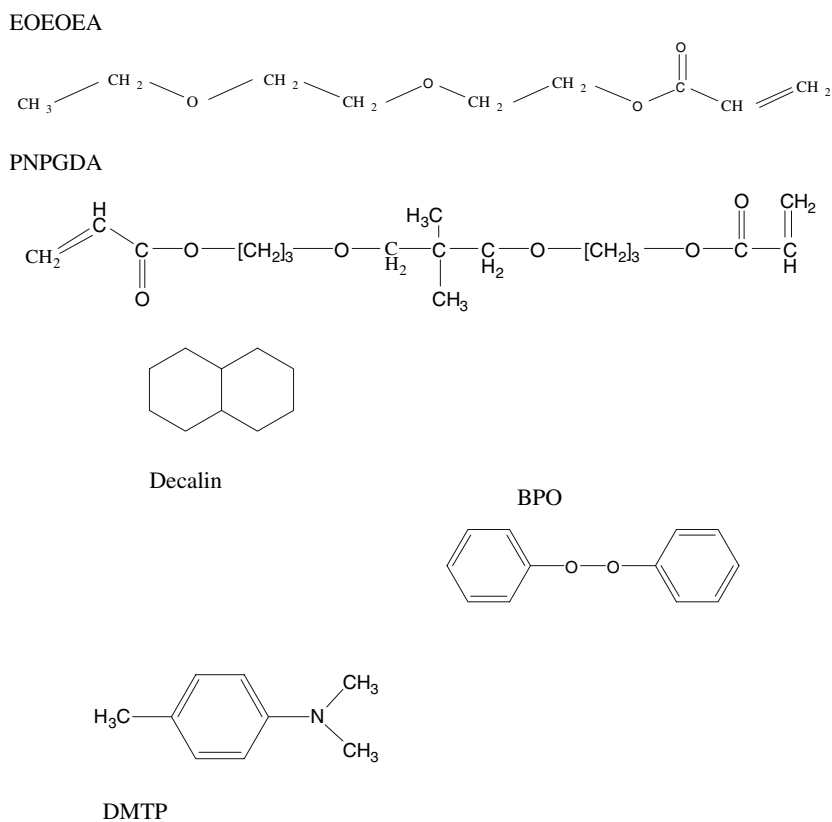
	EOEOEA	PNPDGA
wt.%	96.2	3.8

Table 3 Typical composition of PZT suspension

Chemicals	Composition
PZT856 Powder	51 vol% ($\rho \approx 7.7 \text{ g/cm}^3$)
Monomer Premixture	49 vol% ($\rho \approx 1 \text{ g/cm}^3$)
Dispersant (CC-55)	1 wt% of dried powder
Initiator (BPO)	0.15 wt% of slurry

between the plates. The oscillatory frequency was 1 Hz, and the shear strain was 0.03%, which is in the linear viscoelastic region of the samples. The complex viscosity (μ^*), storage modulus G' and loss modulus G'' could be obtained during polymerization process.

Calorimetric phenomena during polymerization were studied with differential scanning calorimetry (DSC) (DSC-7, Perkin-Elmer, Norwalk, CN). For isothermal mode, heating rate 40 °C/min was used to reach the set temperature point. Since the heating rate was very fast, experimental results showed there was no influence of this heating schedule on curing. When temperature reached set point, few seconds were needed to overcome heating overshoot. For scanning mode, heating rate 5 °C was used.

Fig. 1 Chemical structures of monomers, initiator, diluent, and catalyst

Experimental results

Suspension behavior and chemorheology

The room temperature steady shear viscosity vs. shear rate appears in Fig. 2 for suspensions with 50–54 volume percent PZT. These suspensions are shear-thinning at low shear rates. At a shear rate of 10 s^{-1} , the viscosity for a 51 vol% slurry is 1.8 Pa.s, which is fluid enough for convenient casting. Figure 3 shows typical oscillatory measurement data for storage modulus G' and loss modulus G'' vs. time at 90°C for a monomer with 25:1 monofunctional:difunctional ratio, and the corresponding data for the gelation of a 51 volume percent suspension in this same monomer. The gel point for our purposes was taken to be the time at which the storage modulus G' reached 10 Pa. The ceramic powder-filled suspensions had a rapid rise in G' , and the time where $G' = 10 \text{ Pa}$ was close to the crossover time (where $G' = G''$), which is commonly chosen as the gel point for polymers [21–23] and colloidal gels [24, 25]. This simple criterion was more convenient than extrapolation methods [26, 27]. Gelation is faster in the presence of PZT powder. At 90°C , the gelation times for monomer solution and PZT suspension are 120 and 60 s, respectively. At other temperatures, the same trend was observed. Moreover, PZT powder increases the storage modulus from the 10^5 to 10^7 Pa. This result is reasonable because PZT powder will be entrapped in the polymer network and adsorbed on the polymer chain surface. Figure 4 shows suspension gelation times for different monomer compositions. At low temperature (60 and 70°C), the increase in monofunctional monomer slows the gelation, while at high temperatures (80 and 90°C), the

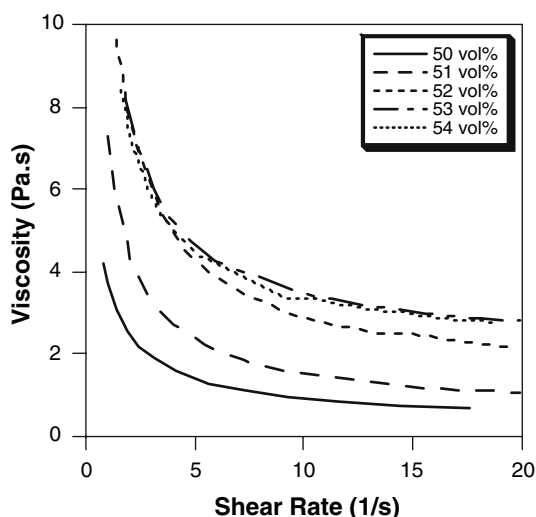


Fig. 2 Solid loading effect on viscosity. Dispersant amount is 1 wt% of powder

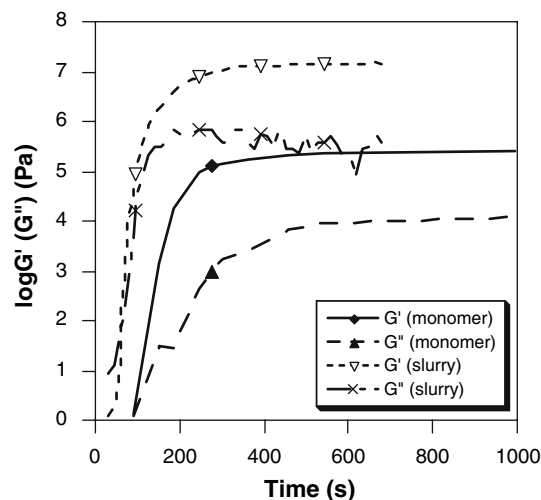


Fig. 3 Gelation process for monomer solution and PZT suspension. Monomer ratio is 25:1, initiator amount is 0.15 wt% of suspension, and temperature is set at 90°C

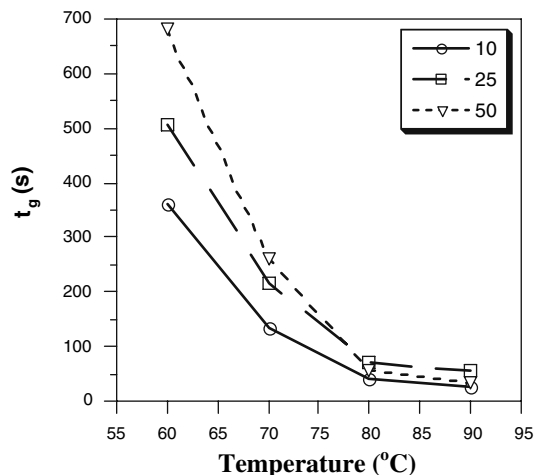


Fig. 4 Gelation time for PZT suspensions with different monomer ratios (EOEOEA/PNPDGA): 10, 25 and 50. Initiator amount is 0.15 wt% of suspension

composition effect is small because the gelation rate is very fast for all monomer ratios. Since $80\text{--}90^\circ\text{C}$ was used in the application, therefore, the monomer ratio had no impact on gelation times. However, the monomer ratio does have a big impact on the network strength, i.e., the more di-functional monomer (crosslinker) added, the stronger the network. However, with more crosslinker, the friction between the green body and mold becomes higher, thus demolding becomes difficult. While with less crosslinker, the network will be softer, and the green body can be distorted during demolding and post handling. Therefore, appropriate amounts of di-functional monomer should be used. In this study, unless otherwise noted, the mono:di-functional monomer ratio 25:1 was used.

Figure 5 shows the effect of initiator concentration on the suspension gelation. At low temperatures, the difference is evident: at 60 °C, the gelation time is about 750 s for 0.1 wt% initiator, 500 s for 0.15 wt% and 300 s for 0.2 wt%. The catalyst DMPT was used to shorten the gelation time and lower the gelation temperature. The catalyst effect is so great that only small amounts (less than 0.1 wt%) of catalyst increase the reaction rate by several hundred percent. With catalyst, initiator decomposition is accelerated, and more radicals are formed. Figure 6 compares gelation with initiator only, and gelation with initiator and catalyst. At 60 °C, the suspension with the catalyst takes about 120 s for the reaction to take place, while with only the initiator takes 500 s to start the reaction. For convenient processing, about 10 min are needed for casting operation. To extend the gelation start time the gelation system was cooled with ice water before casting.

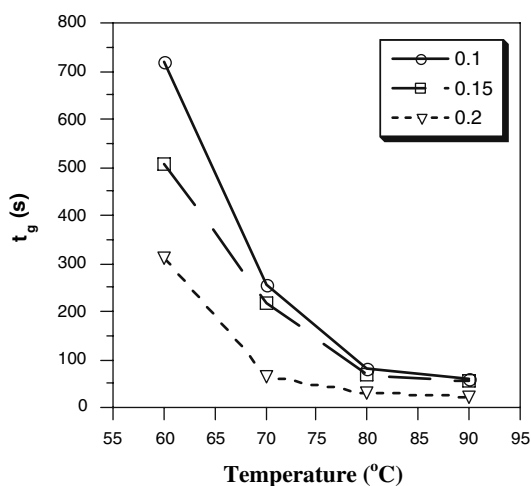


Fig. 5 Gelation time for PZT suspension with different initiator amount: 0.1, 0.15 and 0.2 wt% of suspension

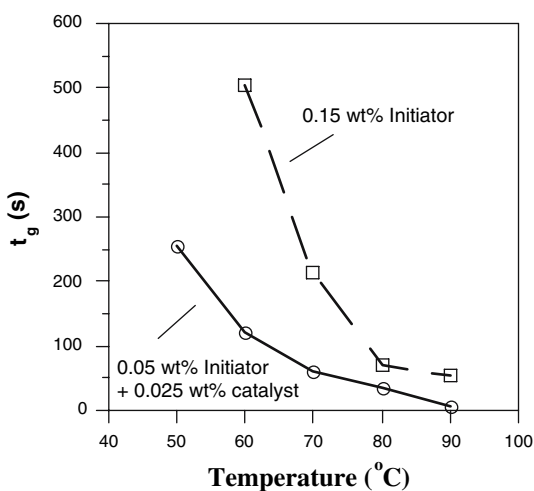


Fig. 6 Catalyst effect on PZT suspension gelation

Addition of decalin as a solvent in the monomer makes subsequent binder burnout much easier [28], so we investigated the impact of decalin on gelation. The effect of decalin on gelation is shown in Fig. 7. Decalin has little effect on monomer solution gelation at low temperatures (60 and 70 °C); but at high temperatures, decalin slows gelation. For the gelation of the suspension, decalin significantly increases gelation time. Moreover, it should be noted that the storage modulus of decalin system is lower than that without decalin, which implies that the network strength is weakened by adding decalin.

Calorimetry

The enthalpy for complete polymerization of the 25:1 EOEOAE:PNDGA monomer system has not been

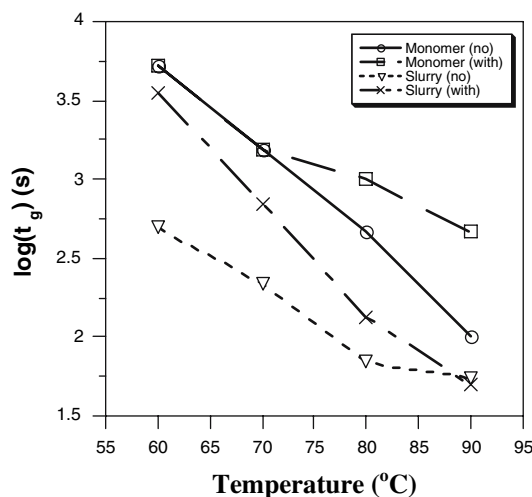


Fig. 7 Gelation time for monomer solution and PZT suspension, with and without decalin at 15 wt% of monomer solution

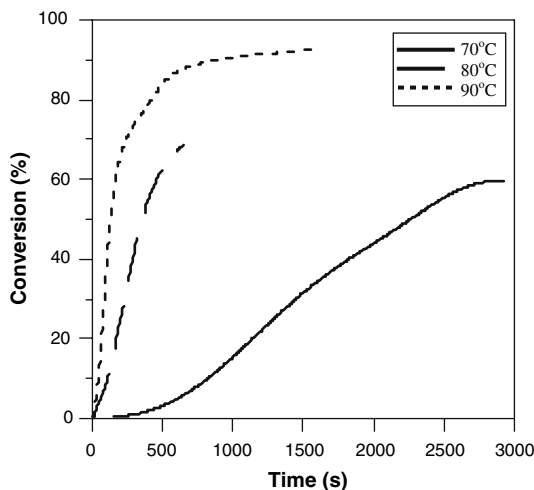


Fig. 8 Monomer conversion for monomer solution without decalin. Monomer ratio is 25, initiator amount is 1.5 wt%

reported, so a calibration scan was conducted using standard methods [24] to establish an enthalpy of 320 J/m^2 for complete polymerization of this system. This is smaller than the value reported by Chu [13] for isobornyl acrylate with PNPdGA. We use the 320 J/m^2 value to calculate extent of reaction from heat evolution.

A typical DSC thermogram for the monomer solution (without PZT powder) appears as Fig. 8. It follows the usual sigmoidal behavior where the monomer conversion increases to the point where further reaction is “frozen” by gelation. At 90°C , the final conversion is about 90%, leaving about 10% residual unreacted monomer. The final conversion is smaller at lower temperatures, reaching 70% at 80°C and only 60% at 70°C . The DSC thermograms for conversion vs. time are similar for the other cases, so will only present final monomer conversion vs. temperature. Figure 9 compares the final conversion for the monomer solution with the PZT suspensions, showing that the suspension consistently achieves high conversion. Figure 10 shows the influence of the monofunctional:difunctional ratio. At lower temperature, conversion is smaller in solutions with more difunctional monomers, although at 90°C all reach more than 90% conversion. Higher concentrations of benzoyl peroxide initiator decreases the extent of reaction, as shown in Fig. 11. Finally, we examined the influence of decalin, which is added as an inert diluent. Recall that decalin appeared to retard gelation in the chemorheological data. However, Fig. 12 shows that decalin does not decrease the monomer conversion. This suggests that it serves as plasticizer, reducing the storage modulus G' , and therefore apparently retarding the gelation onset when gelation is defined as $G' = 10 \text{ Pa}$.

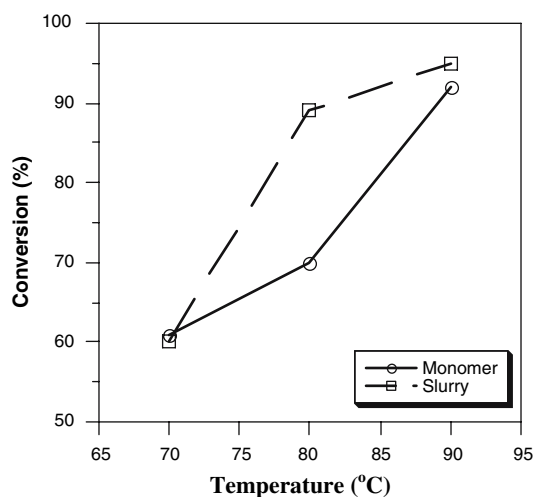


Fig. 9 Monomer conversion for monomer solution and PZT suspension without decalin. Monomer ratio is 25, initiator amount is 0.15 wt% of suspension

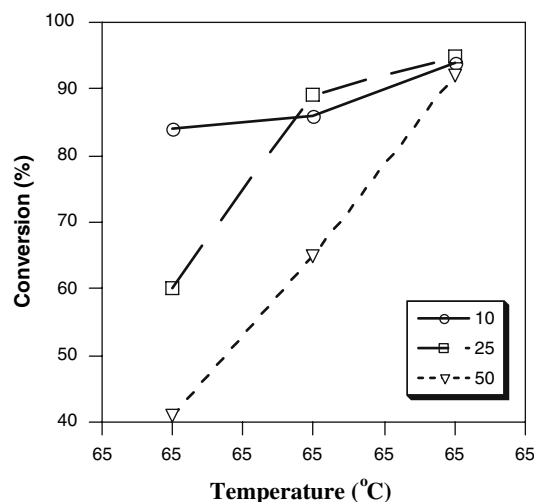


Fig. 10 Monomer conversion for PZT suspension with monofunctional/difunctional ratios of 10, 25 and 50, as wt. EOEOEOEA/wt PNPdGA

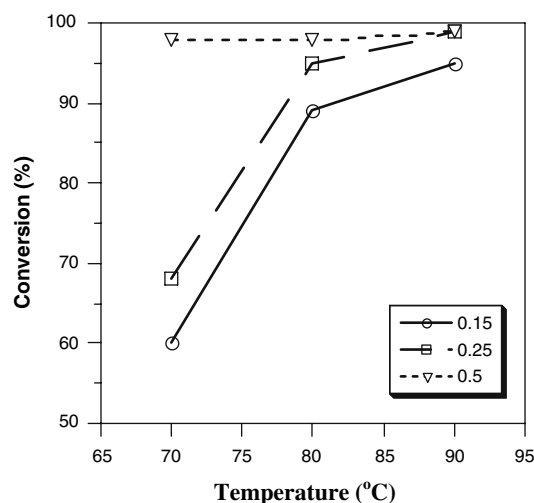


Fig. 11 Monomer polymerization by DSC for PZT suspension with different initiator amount: 0.15, 0.25, and 0.5 wt%. Monomer ratio is 25

Discussion

Temperature dependance of gel point

The temperature dependence of the gel point was investigated by plotting the chemorheological gel time t_g against temperature in an Arrhenius plot, as shown in Fig. 13. There are only four data points, but they roughly fit a straight line, providing the apparent activation energies listed in Table 4. The activation energy of the monomer solutions were about 140 kJ/mole . The activation energy was notably smaller in the presence of PZT powder, centering around 100 kJ/mole for the combinations of monomer ratios and initiator concentrations. Note that the

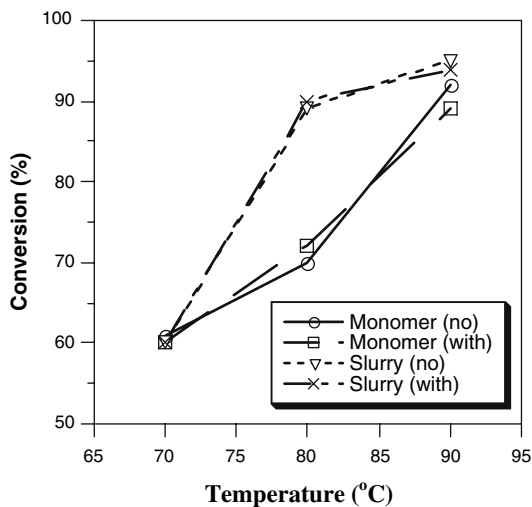


Fig. 12 Conversion for monomer solutions and slurries with and without decalin. For the case with decalin, the decalin amount is 15 wt% of monomer solution

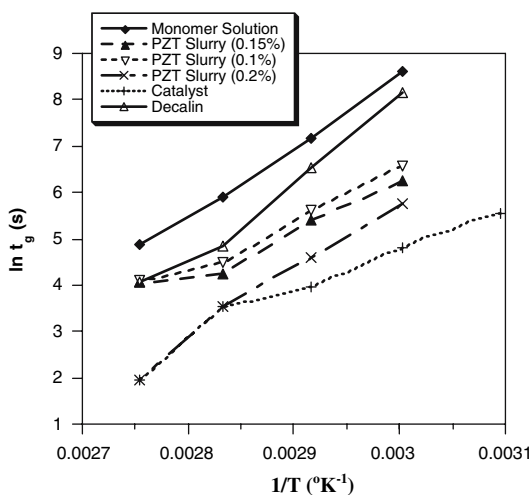


Fig. 13 Gel time from chemorheological measurements versus temperature

Table 4 Apparent activation energy for different from chemorheology

System	Activation energy (kJ/mol)
Monomer solution with 1.5 wt% initiator	132 ± 6
PZT suspension with 0.1 wt% initiator	101 ± 15
PZT suspension with 0.15 wt% initiator	98 ± 20
PZT suspension with 0.2 wt% initiator	108 ± 17
PZT suspension with 0.05 wt% initiator and 0.025 wt% catalyst	64 ± 18
PZT suspension with 15 wt% decalin in monomer	162 ± 21

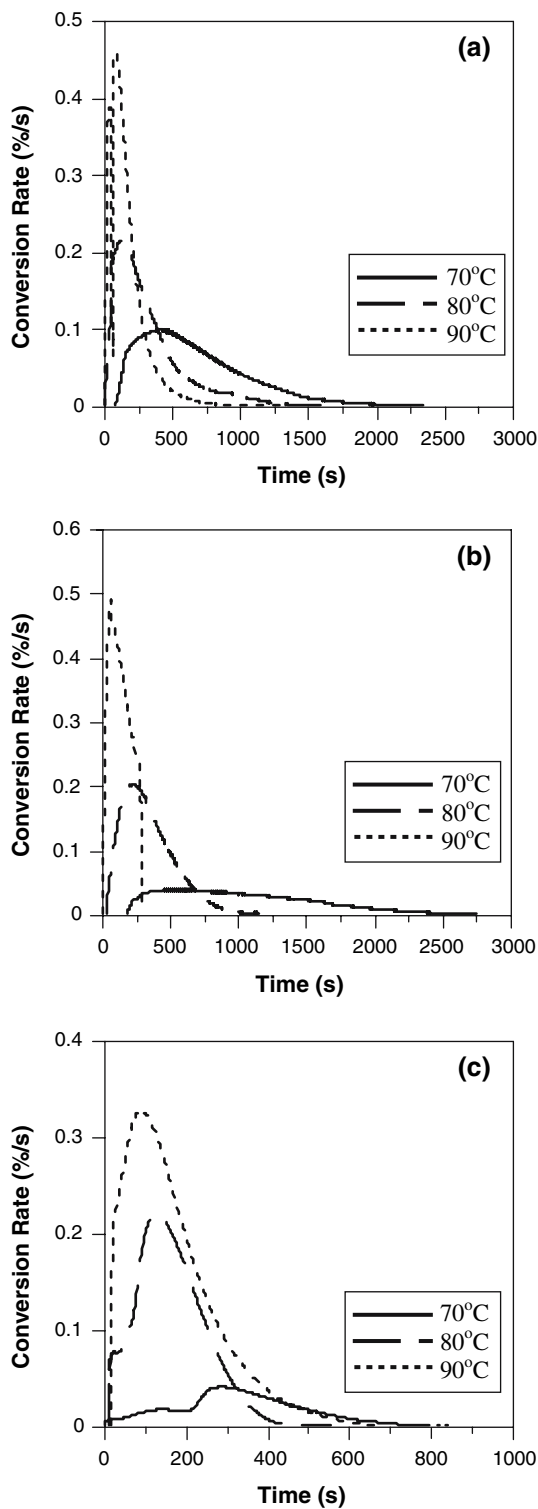


Fig. 14 Effect of monomer ratio on conversion rate. Monomer ratios: (a) 10, (b) 25, (c) 50

suspensions with DMPT catalyst had markedly smaller apparent activation energy, around 60 kJ/mole. The suspensions with decalin seemed to have a larger temperature

Table 5 Kinetic Exponents from DSC

System	m			n		
	70 °C	80 °C	90 °C	70 °C	80 °C	90 °C
Monomer solution with initiator 0.15 wt%	0.82	0.76	0.83	1.18	1.24	1.17
PZT suspension with monomer ratio 25	1.08	0.91	0.97	0.92	1.09	1.03
PZT suspension with monomer ratio 10	0.85	0.89	0.92	1.15	1.11	1.08
PZT suspension with monomer ratio 50	1.03	0.71	0.96	0.97	1.29	1.04
PZT suspension with initiator 0.25 wt%	0.86	0.94	0.90	1.14	1.06	1.1
PZT suspension with initiator 0.5 wt%	0.83	0.78	0.81	1.17	1.22	1.19
PZT suspension with 15 wt% decalin in monomer solution	0.76	0.83	0.79	1.24	1.17	1.21

dependence, although the data points do not make a convincing fit to Arrhenius behavior.

Adding PZT powder increases the reaction rate, which may be attributed to catalytic effects of the PZT powder. Filler content has been shown to decrease reaction rate in polyesters and epoxy resins [16–18], although others report faster reaction in the presence of fillers [29], so the literature suggests the filler effects are not simple. Physically, filler should retard the mobility of free radicals, act as heat sink in the system, and moreover, dilute the overall monomer concentration in the system, all tending to slow the reaction rate. Chemically, some fillers can be inert and not change polymerization kinetics, but others can catalytically promote initiator decomposition and monomer polymerization. Brady and Halloran reported that Al_2O_3 powders had no effect on the *photopolymerization* rated in 1,6-hexanediol diacrylate (HDDA) and 2-phenoxyethyl acrylate (POEA) systems [30]. However, Chu showed that the addition of Al_2O_3 and hydroxyapatite powders increases the *thermal* polymerization rate isobornyl

acrylate (IBA)/propoxylated neopentyl glycol diacrylate (PNPGDA) system [13].

The overall activation energy for this monomer solution without PZT is about 132 ± 6 kJ/mol, which agrees well with Chu [13]. This value is close to the activation energy for initiator (BPO) decomposition (126 kJ/mol) [31]. In the presence of PZT powders, the overall activation energy decreases to about 100 kJ/mol (with 0.15 wt% initiator). Chu showed that the activation energy decreases from 133 kJ/mol in the monomers to 74 kJ/mol and 78 kJ/mol with the addition of Al_2O_3 and hydroxyapatite powder, respectively.

Polymerization Kinetics

The polymerization rate can be fit to a semiempirical kinetic equation of the form [21]:

$$\frac{d\alpha}{dt} = (k\alpha^m)(1 - \alpha)^n$$

where α is the degree of conversion, $d\alpha/dt$ is the conversion rate, k is a kinetic rate constant, m and n are polymerization reaction orders [17, 21, 32]. Following standard procedures, the kinetic constants can be obtained from peak in the kinetic curve from:

$$\alpha_p = \frac{m}{m + n}$$

$$m + n = 2$$

$$\left(\frac{d\alpha}{dt}\right)_p = k \frac{m^n n^n}{(m + n)^{m+n}}$$

where α_p is the degree of conversion at the exothermic peak, $(d\alpha/dt)_p$ is the conversion rate at the exothermic peak. A typical conversion rate diagram for different comonomer ratios is shown in Fig. 14. Table 5 lists the calculated m

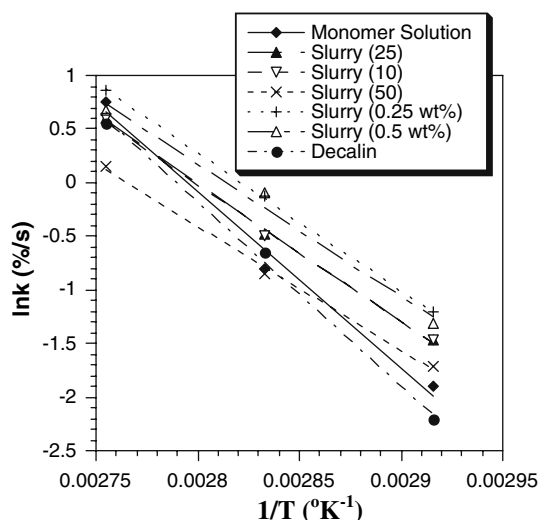


Fig. 15 Polymerization kinetic rate constant inferred from DSC data versus inverse temperature for a variety of systems

Table 6 Apparent activation energy from DSC kinetic data

System	Overall activation energy (kJ/mol)
Monomer solution with initiator 0.15 wt%	137 ± 13
PZT suspension with monomer ratio 25	107 ± 10
PZT suspension with monomer ratio 10	107 ± 10
PZT suspension with monomer ratio 50	97 ± 10
PZT suspension with initiator 0.25 wt%	107 ± 10
PZT suspension with initiator 0.5 wt%	103 ± 10
PZT suspension with 15 wt% decalin in monomer solution	143 ± 14

and n values for different systems. Figure 15 displays the kinetic constant, k , against temperature as an Arrhenius plot, with the apparent activation energies shown in Table 6. The apparent activation energies from the DSC kinetics agree quite well with the independent values from chemorheology. The addition of decalin does not change final conversion, and does not change the activation energy inferred from DSC kinetics. This suggests that high apparent activation energy suggested by chemorheological gel is probably an artifact of choosing t_g as a particular threshold value of $G' = 10$ Pa. The decalin, in its role as plasticizer, decreased the G' and artificially increased the apparent gel time.

Conclusions

Suspension polymerization casting of lead zirconate titanate (PZT) can be accomplished by the polymerization of a 51 vol% suspension of PZT in an ethoxyethoxyethyl acrylate-based system. The polymerization process was characterized with chemorheology and differential scanning calorimetry to determine the influence of temperature, monofunctional and difunctional monomer ratio, inert solvent concentration, initiator concentration, and catalyst. The PZT powder accelerates the acrylate polymerization, decreasing the activation energy for polymerization from 132 ± 6 kJ/mol to 98 ± 20 kJ/mol. Polymerization is faster when the difunctional monomer propolyated neopentyl glycol diacrylate is present at higher concentration. As an

inert solvent, decahycrophthalene does not change polymerization kinetics, but acts as a plasticizer to increase the gel time.

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