Cure cycle optimization of an inorganic polymer matrix material for high temperature fiber reinforced composites

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ABSTRACT

We investigated the potential effects of inorganic polymer processing conditions on the residual stress generation of fiber reinforced inorganic polymer matrix composites. By optimizing various stages of processing it was found that process-induced shrinkage can be reduced by as much as 20%, while simultaneously, the compression strength can be improved by over 30% compared to baseline processing parameters. Further with the optimization of the process parameters, the pore diameter reduced by over 65%, while the relative density increased by a little over 5%. These results suggest high temperature dimensional stability and reduced pore content. Also SEM images indicate a continuous thermodynamic transformation in the bonding strength between the precipitated particles. Thus, it is demonstrated that, through the process modification, a path exists to reduced cure shrinkage, high mechanical strength and thermodynamic stability that results in a potential reduction in residual stresses in continuous fiber reinforced, inorganic matrix composites.

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1. Introduction

The cure cycle optimization of the polymer matrix is an important parameter for fiber reinforced composites to be used in structural application at room as well as elevated temperatures. The cure cycle optimization reduces the shrinkage as well the porosity in the matrix materials that ultimately results in the reduced residual stress and enhanced dimensional stability and mechanical and physical properties in the fiber reinforced composite.

Inorganic polymers typically known as geopolymers, processed at relatively low temperature, offer the potential to cross the process/performance gap as the matrix of a high temperature continuous fiber reinforced composites, offering both simplified processing and elevated temperature functionality. Researchers have produced and evaluated fiber reinforced composites fabricated with these materials as the matrix and have demonstrated reasonably good structural properties, but unfortunately, applications are often limited by toughness. There has been some research suggesting that toughening mechanisms, which are successful for both ceramic matrix composites and polymer matrix composites are effective in these inorganic polymer matrix composites [1,2]. However, processing studies have shown that the shrinkage typically associated with the cure of these inorganic polymers, has

led to residual stresses in the composites and to internal cracking [3]. Thus, there is a need to optimize the cure cycle and investigate its effect on shrinkage and the evolution of mechanical properties and their correlation with microstructural changes.

The inorganic polymer under the current investigation is described as a polysialate ceramic [4], which is formed by polycondensation reaction with a specific ratio of Si:Al and the proportions of K_2O/SiO_2 and H_2O/Na_2O. Polymerization of these inorganic polymers is the result of a polycondensation reaction, which requires an ionic balance of the sialate network in the presence of positive alkali ions (Na^+, K^+ and Cs^+, etc.). The corresponding empirical formula for the inorganic polymer is;

$$M_n\left\{-(SiO_2)_Z - (AlO_2)\right\}_n \cdot wH_2O \qquad (1)$$

where M is the alkali cation, z is the ratio of Si:Al, n is the degree of polymerization, and w is the number of water molecules [5]. The chemical backbone of inorganic polymer is formed in a tetrahedral network of Alumino-Silicate [6], which is made of SiO_4 and AlO_4 covalent structures, bonded by oxygen atoms in an alternating fashion.

Low temperature processing capability of inorganic polymer suggests the similarities in the processing schemes between the inorganic and organic polymer materials. This capability enables good wet out of the reinforcing fibers and thus improves fiber–matrix interface in the continuous fiber reinforced composites. However, process related cure shrinkage which often develops

residual stress in the fiber reinforced thermosetting polymer composites [3,7–9], can also develop similar residual stress in the inorganic polymer matrix composites. Several studies have shown that during the cure process this stress develops at the gelation point [10–12], and increases substantially at the point of vitrification, which can result in the distortion of composites and matrix cracks [13]. With the more brittle ceramic-like properties, residual stress induced crack development can be even more detrimental to the inorganic polymer matrix composites. Therefore, it is crucial to reduce shrinkage during the cure process.

Researchers have reported the optimization of mechanical and thermal properties of inorganic polymer by tailoring Si:Al, Na:Al and $Na_2O:H_2O$ ratios [14–16] and adding reinforcing fibers and fillers [17–19]. Majority of those efforts were found on inorganic polymer as the high temperature coatings [20] and the replacement of ordinary port-land cements [21]. However, limited initiatives [22,23] have been made on understanding the ability to limit shrinkage of inorganic polymer by optimizing the cure cycle. Also, minimum efforts have been found to establish these materials as the matrix of a continuous fiber reinforced composites. Therefore, the goal of our efforts is to optimize the processing parameters of this polymer as a viable/successful matrix material for continuous fiber reinforcement composites. In our previous effort [24], the process schedule was optimized by varying time and temperature. The process induced shrinkages obtained from the various process schedules were sub-divided into three primary forms, which are (i) curing, or poly-condensation, (ii) drying, and (iii) diffusion. Adequate humidity was maintained during the cure stage in order to reduce the shrinkage of the inorganic polymer by ensuring the completion of crosslinking during the poly-condensation reaction [24,25]. However, both process related shrinkage and mechanical strength is expected to have strong correlation with the microstructure. The goal of the current effort is to correlate the results obtained from the studies [24] related to the shrinkage and mechanical properties to the changes in the inherent microscopic porosities and microstructure with the variations in the process schedule. Thus, the current study was initiated to investigate the effects of varying the processing conditions, understanding the physical states of the materials determining suitable parameters to successfully produce neat inorganic polymer matrix specimens to gain an improved understanding on the performance of the fiber reinforced geopolymer composites.

2. Experimental

2.1. Materials

The trade name of the geopolymer utilized throughout this work is MEYEB (supplied by Pyromeral systems Inc). It is a Potassium balanced, polysialate [4] with the ratio of Si:Al of 1:1 and proprietary proportions of K_2O/SiO_2 and H_2O/K_2O. MEYEB is supplied in the form of a slurry, which consists of various chemicals including potassium silicate, aluminum oxide, silicon dioxide, aluminum phosphate and water.

2.2. Specimen preparation

The goal of this effort was to reduce shrinkage induced cracking during processing, which had been an impediment to realizing toughness improvements in the resulting fiber reinforced composites during previous laboratory experiments. To evaluate the potential to reduce process-induced residual stresses, neat resin specimens were prepared for the measurement of shrinkage during cure and postcure, and for the evaluation of the response of the resulting mechanical and physical properties. Tests were developed to evaluate the response, related to each of the stages of processing, including varying the cure time for poly-condensation and the heating rates, dwell times and temperatures for the drying stage of the process. Tests were performed in two series, first evaluating the effect of initial cure time, prior to drying, on the poly-condensation reaction, and then in the second series, measuring the results after various drying and postcure schedules, as described in Table 1.

The first series of test specimens were cured in a sealed environment to ensure that moisture was retained, not allowing the specimens to prematurely dry. This group of specimens was cured at 80 °C for times ranging from 1 h to 30 h. The second series of tests was designed to study the effects of variations in cure and drying schedules. The details of the process schedules used for this second series of trials are given in Table 1. Trials are labeled 'A' for cases with initial cure stage of 10 h or less and are labeled 'B' to represent cases where this stage was extended to 24 h. Drying parameters varied with the specific case being considered. The 650 °C postcure was held constant, throughout all trials. Linear shrinkage and compression strength were measured to assess the effects of varying the process parameters. A minimum of five specimens were produced for each condition evaluated. Specimens were prepared in a sealed environment to ensure moisture retention. Details can be found in Ref. [24].

3. Characterization technique

3.1. Evaluation of the process variations

To evaluate the effects of the process cycle variations, process-induced shrinkage and the resulting mechanical properties were measured using the specimens treated at each stage of the process. Process-induced shrinkage is a major factor in the development of

Table 1
Cure schedule, series 2.

Sch. name	Cure 80 °C (h)	1st stage				2nd stage	3rd stage
		Drying 80 °C (h)	Evaporation hold (h)			250 °C (R-1 °C/min)	Post cure hold (h)
			100 °C (R-0.1 °C/min)	145 °C (R-1 °C/min)	175 °C (R-1 °C/min)		650 °C (R-5 °C/min)
A-1	2					5§	5
A-2	10	0.2				5§	5
A-3	10	2	3	3		5§	5
A-4	10	10	3			5	5
A-5	10	10	3	3		5	5
A-6	10	10	3		3	5	5
B-1	24	10	3			5	5
B-2	24	10	3	3		5	5
B-3	24	10	3		3	5	5

R – ramp.
§ For A-1, A-2 & A-3, the heating rate is 5 °C/min for heating to 250 °C.