



Controlled degradation of disulfide-based epoxy thermosets for extreme environments



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ABSTRACT

The burgeoning field of smart materials for oil exploration and production (E&P) demands robust polymers that remain stable in extreme conditions, but readily respond to specific chemical cues. Here, disulfide-based epoxy polymers are designed to withstand harsh, simulated oil reservoir conditions while simultaneously retaining the ability to degrade from thiol compounds. Degradable epoxy thermosets are prepared by using Bisphenol-F diglycidyl ether (BFDGE) in combination with blends of p,p'-diaminodicyclohexylmethane (PACM) and 4-aminophenyl disulfide (4APDS). These polymer systems retain their mechanical properties after exposure to extreme conditions (e.g., two weeks, 69 MPa, 100 °C, pH 12), but degrade in the presence of 2-mercaptoethanol (2-ME). Parameters that influence polymer degradation are detailed including temperature, concentration of disulfide groups, and monomer stoichiometry. Formulations that entirely dissolve after exposure to 2-ME are utilized further for release of prototype tracers. Disulfide-based epoxy thermosets provide a unique platform for applications in harsh environments requiring robust materials capable of on-demand degradation.

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1. Introduction

The design and utilization of innovative polymeric materials is the mainstay for solving numerous challenges in the petroleum industry. Polymers have been used to eliminate insoluble inorganic salt deposition on surfaces of production conduits (i.e., scale formation) [1], to prevent excess water waste during oil recovery (i.e., water shutoff) [2,3], and to moderate bacterial growth to prevent accumulation of deleterious metabolites (e.g., hydrogen sulfide) [4]. Recently, an innovative research direction involves the design of stimuli-responsive polymeric materials for oil E&P that are capable of characterizing specific reservoir properties and delivering chemical agents. For instance, these new materials include carbon black nano-reporters for hydrocarbon detection [5], polymer functionalized magnetic nanoparticles for characterization of sub-surface topography [6], and stimuli-responsive polymer microcapsules for chemical delivery [7,8]. Many of these systems integrate specific chemical cues within the material that respond to environmental stimuli and perform pre-programmed functions,

such as delivering chemical cargo or tracking migration history through rock formations [9–13].

The new stimuli-responsive materials used in oilfield applications must function under the demanding environments of sub-surface terrains where extreme temperatures, pressures, and salinity are commonplace. Although conditions vary widely depending on geography and depth, reservoirs contain both oily and aqueous regions that often exceed 35 MPa and temperatures of 100 °C and beyond [14]. The requirement of materials to sustain structural integrity under these harsh conditions necessitates the design of material with unique properties that differ from many current stimuli-responsive materials used in mild environments, such as biological systems [15]. To support smart materials for energy applications, there exists a need for continued advancement of materials capable of enduring these extreme reservoir conditions while responding to a specific chemical cues to perform an appropriate function.

One material class with great benefit for extreme environments is the epoxy thermosetting resins. The utility of epoxy thermosets spans various applications that require robust materials, including aerospace operations [16], microelectronics [17], automotive manufacturing [18], and biomedical device fabrication [19,20]. The petroleum industry has also employed epoxy-based materials to

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coat pipelines [21] and to reinforce drilling wells [22,23]. This overall versatility originates from the beneficial properties inherent to many epoxy systems, including thermal stability, excellent adhesion, and mechanical strength. Moreover, the minimal ease during handling and low volatiles during processing is attractive for needs in manufacturing scale-up and industrial operations. Epoxy materials can exhibit high monomer conversion resulting in tightly crosslinked networks with resilience to many solvents and capable of withstanding demanding environments.

The design of many stimuli-responsive thermosetting materials, such as epoxy systems, often requires the incorporation of specific cleavable crosslinks. For epoxy thermosets, the removal and degradation of the material often proves challenging owing to the inherent strength and stability of cured epoxy resins. For example, the removal of cured epoxy resins from substrates typically involves non-specific approaches such as solvent treatments (e.g., methylene chloride, toluene, sulfuric acid), photolytic bond scission [24] or applied mechanical force. An alternative approach for degrading cured epoxy resins involves a ‘command-destruct’ method [25], wherein an extraneous trigger selectively degrades the material. To achieve controllable degradation profiles, the material is often prepared with monomers containing chemical functional groups that degrade in response to a chemical or thermal trigger. For example, monomers containing acetal and ketal functional groups were used to prepare epoxy thermosets capable of degrading in the presence of acidic solvents [25,26]. Additional degradable epoxy systems have incorporated Diels–Alder adducts within the network that de-crosslink at elevated temperatures via cycloreversion of maleimide and furan side groups [27–30]. Other systems have incorporated sulfite [31], carbamate [32], carbonate [33], tertiary esters [34], or phosphate [35,36] groups into the epoxy polymer to facilitate degradation reactions.

Another beneficial chemical approach for controlling the breakdown of the epoxy structure involves thiol-disulfide interchange chemistry [37], where disulfide groups integral to the epoxy thermoset cleave specifically in response to a thiol compound. Pioneering work by Tesoro et al. demonstrated the ability to incorporate disulfide degradable crosslinks into an epoxy network for recovery and reuse of epoxy materials [38–40]. Under specific crosslinking densities and sample surface areas, disulfide-containing epoxy thermosets readily degrade in the presence of thiol compounds [39,40]. To date, however, the ability to guide degradation kinetics of the epoxy thermoset by controlling the disulfide content has not been investigated. Moreover, evaluating the durability of this material after exposure to challenging environmental conditions (e.g., high pressure, salinity, and temperature) is essential for use as stimuli-responsive materials for E&P technologies or alternative demanding applications.

Continued advancement of technologies for E&P requires further development of smart materials capable of withstanding harsh conditions while simultaneously maintaining function and sensitivity to specific, programmed cues. In this study, we demonstrate that disulfide-containing epoxy materials may support this need and hold value for the emerging area of smart materials for energy applications. Herein, we show the ability to control the degradation of epoxy thermosets, which are otherwise stable in harsh, simulated reservoir conditions, by using a specific thiol trigger. This report details the parameters that dictate the degradation kinetics including temperature, concentration of disulfide groups, and monomer stoichiometry. We anticipate that incorporating disulfide moieties integral to an epoxy resin will benefit various industries that require robust materials capable of on-demand degradation, recycling applications, and self-healing capabilities.

2. Experimental

2.1. Sample preparation and thiol exposure studies

Samples were prepared by combining the BFDGE epoxy monomer (epoxide equivalent weight of 169 (Momentive)) with appropriate amine monomer (PACM with amine hydrogen equivalent weight of 52.5 (Air Products) or 4APDS with amine hydrogen equivalent weight of 62.1 (TCI)). Samples contained either a stoichiometric ratio of monomers (i.e., 1:1 M ratio of amine hydrogens:epoxide groups) or an off-stoichiometric ratio of monomers (i.e., 1.5:1 M ratio of amine hydrogens:epoxide groups). Blends of 4APDS and PACM, in combination with BFDGE, were prepared according to weight percent (e.g., 100:0, 75:25, 50:50, 25:75, 0:100 weight percent of 4APDS:PACM). If 4APDS was required for a formulation, it was dissolved with BFDGE using heat and subsequently cooled before adding the PACM monomer. After the combined monomers were thoroughly dissolved, the samples were subsequently degassed by vacuum. All material in this manuscript was used as received without further purification.

DMA bars were prepared by pouring the pre-mixed monomers into in-house fabricated aluminum molds containing DMA bar slots with dimensions of 35 mm × 12.7 mm × 2.6 mm. Before pouring the resin, the aluminum molds were coated with FreKote 700-NC release agent. All samples were cured at 80 °C for 60 min followed by 150 °C for another 120 min. For the solvent exposure studies at ambient pressure, cured epoxy sample bars (same dimensions as the DMA bar slots) were placed into 20 mL of 100% of 2-ME (Aldrich) and incubated at 25 °C or 80 °C for a designated time. The weight of the specimens were acquired before (W_0) and after immersion into the solvent (W). After removal from the solvent, the surfaces of the samples were dried prior to weighing by gently wiping the surface. The percentage of weight change ($\%W_{\Delta}$) was calculated using the formula:

$$\%W_{\Delta} = [(W - W_0)/W_0] \times 100$$

2.2. High pressure high temperature (HPHT) studies

HPHT experiments were performed using a Fan Model 275 consistencyometer. Epoxy sample bars were immersed either into a retarded cement slurry of pH = 12 (4% cement retarder) or 100% refined mineral petroleum oil (Ibex Chemicals, Inc.) and loaded into the HPHT chamber. The samples were maintained at 69 MPa and 100 °C for either one or two weeks, as indicated. Samples were rinsed with water or acetone and patted dry after removal from the HPHT.

2.3. Characterization

2.3.1. Dynamic mechanical analysis (DMA)

Experiments were performed using a DMA instrument equipped with a single cantilever clamp (Q 800 TA Instruments). DMA tests were performed with a single frequency of 1 Hz and amplitude of 5 μ m. The temperature ramp occurred from 30 °C to 180 °C at 2 °C/min. All DMA experiments were repeated at least three times for each condition. The glass transition temperature was taken from the maximum of the peak in the α -transition region of the tan delta curve.

The molecular weight between crosslinks (M_c) was determined using the following equation:

$$M_c = 3\rho RT/E$$

where ρ = density of the polymer, R = gas constant, T = absolute temperature where the modulus is acquired, and E = storage

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