



Chemical treatment for recycling of amine/epoxy composites at atmospheric pressure

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ABSTRACT

The use of fiber-reinforced composites poses significant environmental problems because most end-of-life composite waste is sent to landfills, and effective recycling technologies have drawn research attention. Our previous study demonstrated that chemical treatments at atmospheric pressure – depolymerization (benzyl alcohol/K₃PO₄ at 200 °C) and acid digestion (acetic acid/H₂O₂ at 110 °C) – were both effective for dissolution of amine-cured neat epoxy. In this paper, depolymerization and acid digestion were applied to amine/epoxy composites, including composites produced from lab-made and aerospace prepregs, and commercial composite waste. Findings indicated that acid digestion was more effective for highly crosslinked amine/epoxy composites than depolymerization. Furthermore, digestion occurred via reaction steps of oxygen atom transfer to the aniline groups and then bond cleavage, resulting in recovery of near-virgin quality fibers at faster dissolution rates and lower temperatures. The relationship between epoxy functionality, fiber bed architecture, fiber reinforcement, laminate thickness and matrix dissolution rate were investigated, and key parameters affecting the dissolution rate were identified. Data showed that the major rate-limiting factor for acid digestion was the diffusion rate, rather than the chemical reaction rate. Two strategies to enhance the diffusion rate – pre-treatment and mechanical shredding – were evaluated, and both were effective. Polymer matrices in pre-treated and shredded composites were homogeneously decomposed in 1 h.

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1. Introduction

The global demand for carbon fiber-reinforced polymers (CFRPs) is expected to grow to 146,000 ton/yr in 2020, consuming 89,000 tons of carbon fiber [1], as the demand for lightweight materials increases. Due to the absence of effective recycling methods, most composite waste is not recycled/treated but is sent to landfills. Without a robust and effective method to recycle composites and complete the material life cycle, composite replacement of metallic parts will be limited in automotive, sporting goods, and energy industries. Consequently, effective recycling methods for CFRPs are required to reduce environmental impact and facilitate entry into sectors requiring mass production.

The objective of this work is to demonstrate and evaluate chemical treatment methods for amine/epoxy composites at atmospheric pressure that can effectively separate fibers and epoxy matrix to near-virgin quality fibers and potentially useful polymer

components. The investigation focuses on amine-cured epoxies, which is the most widely used polymer matrix in high-performance composites [1,2]. A parametric study is performed that encompasses variations in chemical treatment method (depolymerization and acid digestion), matrix properties (epoxy monomer functionality and amine/epoxy molar ratio (A/E)), fiber bed architecture (2 × 2 twill weave and unidirectional (UD) fibers), and fiber type (carbon fiber (CF) and glass fiber (GF)). Key factors affecting the recycling process are identified and modified to accelerate the separation process. The long-term goal of the recycling project is to develop a catalytic method for cleavage of amine/epoxy molecules using moderate conditions (atmospheric pressure and moderate temperature) and safe chemicals. These features are critical to practical, large-scale composite recycling to recover long continuous fibers and useful chemical components, but have not been reported to date.

Recycling of epoxy composites presents a daunting challenge because the epoxies are highly cross-linked, three-dimensional structures and are insoluble and under mild conditions [3,4]. Consequently, most efforts to recycle epoxy composites have

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largely focused on recovering the higher value component, the carbon fibers, discarding the polymer matrix. Currently, there are two physical recycling approaches practiced on industrial scales: mechanical grinding [5] and thermal processing [6,7]. The main advantage of physical recycling methods is that composite materials with various matrices and fiber reinforcements can be accommodated by a single process, and tuning these processes to particular matrix formulations is not necessary. However, neither method recovers any of the matrix, and both methods have inherent drawbacks, as outlined below.

Mechanical grinding produces fillers or reinforcement for lower grade composites. Though the mechanical integrity of recycled composites could be improved by careful separation and reincorporation [5], long clean fibers cannot be recovered from grinding, and market demand for ground materials is limited. Thermal processing (pyrolysis) is now the most widely used process in industrial scale recycling. Pyrolysis breaks down polymer matrices into lower molecular weight components, although the temperatures (450–700 °C) can result in fiber degradation and char [6–8]. Analysis of the recovered material showed that pyrolysis above 600 °C caused severe oxidation of the carbon fiber, and the fiber strength decreased by > 30% [6]. Furthermore, pyrolysis of the matrix left residual char on fiber surfaces, and fiber purity was less than the desired level of 99.5% [8]. Fibers recovered from thermal processing are generally chopped into short fibers for use in molding compounds and other applications, and most of the value of the continuous fibers/fabrics is lost. Due to the limited market demand for recycled short fibers, most composite materials are not being recycled today.

Recent recycling research has focused on lab-scale chemical approaches that can recover clean fibers (99.9% purity) [8] with greater than 90% strength retention [9]. For example, supercritical fluids have been evaluated for recycling due to the high mass transfer coefficient and diffusivity. High temperature (>250 °C) and high pressure (>2.5 MPa) were used in experiments to recover fibers from composites (specific reaction conditions depend on the nature of the matrix) [8–14]. However, the aggressive conditions inevitably led to fiber degradation, and the tensile strength of recovered fibers was reduced by 1–15% [10]. Commonly used solvents have included water [10–12], methanol [13], ethanol, propanol, acetone, and their mixtures [14]. Alkaline catalysts, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH), were often added to reaction systems to accelerate the reaction and reduce the reaction temperature [14]. In addition, various metal salts were employed as catalysts to cleave the C–N bonds in epoxy matrices, including AlCl₃, FeCl₃, ZnCl₂, CuCl₂, MgCl₂ [15–17]. Most chemical recycling methods focused on amine-cured bisphenol A type epoxies (bi-functional epoxy) [10–16], which featured relatively low crosslink density and glass transition temperature (T_g). However, Liu et al. investigated a chemical recycling method for CFRPs with high crosslink density ($T_g = \sim 210$ °C) using a ZnCl₂/ethanol system at 180–220 °C [17]. The CFRPs used were manufacturing scraps, and the main composition of the matrix was amine-cured epoxy. Results showed that a matrix degradation degree of ~90% could be achieved.

To date, chemical recycling methods have not been employed on an industrial scale recycling due to 1) the high capital costs associated with high temperature and high pressure conditions, 2) the slow recycling rates and corrosive reaction media, and/or 3) a lack of post-treatment methods for chemical solutions after recycling. There is an urgent need for effective low-pressure methods that require less corrosive reaction media and are readily scalable. The present work demonstrates chemical treatments for amine/epoxy composite recycling that can be performed under atmospheric pressure and moderate temperature (≤ 200 °C).

Chemical treatment methods for thermoset composites at atmospheric pressure have been reported, often using nitric acid [18]. However, strong acid solutions pose environmental hazards, leading researchers to seek methods that require less corrosive reaction media and are safer to handle. For example, Hitachi Chemical reported a solvolytic depolymerization method conducted at atmospheric pressure for anhydride/epoxy systems. The protocol involved using chemical solutions comprised of alkali metal salt (catalyst) and high boiling point alcohol (solvent) [19,20]. However, amine/epoxy formulations lack ester groups for transesterification, a reaction essential to the Hitachi technology. Thus, the solvolytic depolymerization approach cannot be used to dissolve amine/epoxy matrices.

Chemical dissolution of amine-cured epoxy formulations requires a different approach. Oxidative treatment methods using a mixed solution of hydrogen peroxide and organic solvents, such as *N,N*-dimethylformamide [21] and dilute nitric acid [22], were reported to dissolve amine/epoxy matrices. Results showed that clean fibers were separated from the matrix (amine-cured bi-functional epoxy), and the recovered fibers retained >95% tensile strength [21]. However, dissolution of amine/epoxy matrices with higher crosslink density is more challenging, and doing so in oxidative environments has not been considered. Previous work [23–26] demonstrated that both depolymerization (benzyl alcohol/K₃PO₄ at 200 °C) and acid digestion (acetic acid/H₂O₂ at 110 °C) were effective for amine-cured neat epoxy with high crosslink density. The epoxy dissolution rate was controlled by both the chemical reaction rate and the diffusion rate. The reaction mechanism for oxidative degradation of amine-cured epoxies was investigated, revealing that reaction occurred by oxygen atom transfer to the linking amine groups, and the polymers were then cleaved by an elimination and hydrolysis sequence [26].

In this study, we report methods for depolymerization and acid digestion on amine/epoxy composites and compare with similar methods applied to neat epoxy. Composites were fabricated using select epoxy formulations and fiber reinforcements, and subsequently subjected to chemical treatments to identify correlations between epoxy matrix functionality, laminate thickness, fiber bed architecture, fiber type and dissolution rates. Results show that both depolymerization and acid digestion achieve complete matrix dissolution and fibers are recovered. Acid digestion is shown to be a more effective approach for amine/epoxy composite recycling because it offers faster chemical reaction rates at lower reaction temperature, and recovers residue-free fibers. Furthermore, two strategies to improve the matrix dissolution rate – pre-treatment and mechanical shredding – were employed using both laboratory and commercial amine/epoxy composites. Both strategies effectively accelerate the diffusion rate and recover clean fibers.

2. Experiments

Amine/epoxy resins were formulated (without toughening agents or other additives) and characterized using thermal analysis. A total of ten fiber-reinforced composite laminates were fabricated using prepregs that consist of the resin formulations with variations in crosslink density. Samples of composites produced from lab-made prepregs, composites produced from commercial aerospace prepregs (Cycom 5320–1/8HS) and commercial composite waste (provided by ELG Carbon Fibre Ltd.), were subjected to chemical treatment to evaluate speed and effectiveness of dissolution for recycling. Recovered fibers were examined by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) to determine surface quality. Residue on the fibers was analyzed using energy dispersive X-ray spectroscopy (EDS) to determine chemical composition.

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