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Chemical recycling of carbon fibre reinforced epoxy resin composites in subcritical water: Synergistic effect of phenol and KOH on the decomposition efficiency

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ABSTRACT

The combination of phenol and potassium hydroxide (KOH) was used to chemically recycle carbon fibre reinforced epoxy resin cured with 4,4′-diaminodiphenylmethane in subcritical water. This combination had a synergistic effect on decomposing this kind of epoxy resin. The main decomposition products from the epoxy resin were identified by means of GC–MS, and a possible free-radical reaction mechanism for the decomposition of epoxy resin is proposed. The recovered carbon fibres were characterized using single fibre tensile tests, scanning electron microscopy and X-ray photoelectron spectroscopy. Compared to virgin carbon fibres after sizing removal, the surface compositions of the recovered carbon fibres had little change and the tensile strength of the recovered carbon fibres was well retained.

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1. Introduction

Although polymer chemistry provides many methods to synthesize various new polymers, such as plastics and rubbers, it is most desirable to transform waste polymers into potential feedstock through chemical recycling. Thus, the development of an effective method for the chemical recycling of waste polymers is one of the most crucial problems facing the world today. However, owing to chemical and economical issues, it is usually a difficult process to recycle waste crosslinked polymers and their composites. Carbon fibre reinforced resin composites (CFRP) have been widely applied in many fields, such as transport tools and sporting goods, etc., which is ascribed to unique performance of carbon fibre in mechanical properties and corrosion resistance, and so on [1,2]. However, the production of carbon fibre is a high cost process in energy. If carbon fibre with high properties is recycled in an economical way, the recovered carbon fibre can displace pristine counterparts in some applications. As a result, a lot of energy for producing carbon fibre will be saved. So, in order to realize chemical recycling of CFRP efficiently, a key scientific issue is to explore the suitable reaction conditions, under which both recovered carbon fibres and the resultant decomposition products are highly useful and economical.

So far, several recycling technologies for polymer composites have been studied. The main recycling method could be classified into three types, including mechanical recycling [3–5], thermal processing [6–8] and chemical recycling [9–19]. Among them, chemical recycling is an attractive route for decomposing polymer matrices into useful chemicals and avoiding the damage of carbon fibres. Up to now, researchers have used several solvents for decomposing epoxy composites, such as tetralin [9], nitric acid [10,11], supercritical/subcritical alcohols [13,14] and supercritical/subcritical water [15–18].

Considering environmental protection, it is an appropriate way to use water as reaction medium to recycle CFRP compared to using other solvents. Water is a green reaction medium since it is cheap, recyclable, non-toxic and relatively easy to handle. Unfortunately, the previous reports paid a chief attention to the recovered carbon fibres, and the information about the decomposition products of polymer matrices under supercritical/subcritical water has not been reported in detail [15–17]. Addition of acidic or basic compounds in water is necessary to improve the decomposition efficiency. However, strong acidic or basic environments were harmful to mechanical properties of recovered carbon fibres. More recently, Bai et al. recycled carbon fibres from CFRP in supercritical water in the presence of oxygen [17]. They found that oxygen can promote the decomposition of epoxy resin. However, the tensile strength of the recovered carbon fibres decreased rapidly when the decomposition efficiency of polymer matrix was increased to 96.5 wt% above, which was attributed to the excessive oxidation of recovered carbon fibres.

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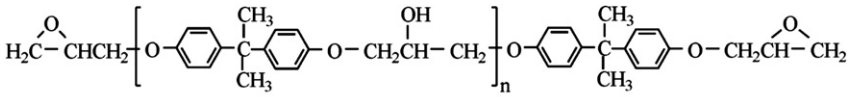
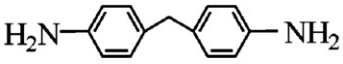
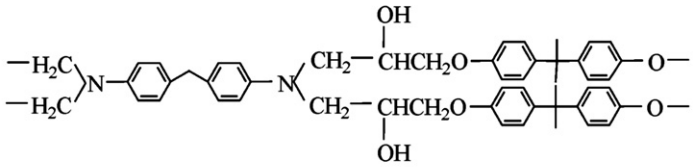


Bisphenol A type epoxy resin



DDM (4,4'-diaminodiphenylmethane)



Bisphenol A type epoxy resin cured with DDM

Fig. 1. Chemical structures of epoxy resin, curing agent and cured resin.

According to the above analysis, it is urgently needed to establish a mildly and efficiently catalytic system in order to decompose CFRP in supercritical/subcritical water and avoid the damage of carbon fibres. Our previous experiments indicated that the decomposition efficiency of CFRP increases slowly with the reaction time at the early stage and then increases rapidly as the reaction time exceeded a critical value using an alkali (e.g. KOH) in subcritical water. The fact that the main decomposition product was phenolic compounds prompted us to consider that the phenolic compounds may accelerate the decomposition reaction of epoxy matrix. Saisu et al. reported that phenol could react with reactive sites during the decomposition of lignin in supercritical water [20]. In this work, the combination between KOH and phenol was used to chemically recycle CFRP in subcritical water. The effects of the combined system on the decomposition efficiency, products of epoxy matrix and the properties of recovered carbon fibres were studied. As expected, the results showed that the combination between KOH and phenol could dramatically promote the decomposition efficiency in the reaction system compared to the one containing KOH alone. The possible mechanism about the synergistic effect between KOH and phenol on the decomposition reaction of epoxy resin was discussed.

2. Experimental

2.1. Preparation of carbon fibre reinforced epoxy composites

CFRP sheets were prepared in the laboratory using a vacuum bagging technique. The matrix resin used in this study was diglycidyl ether of bisphenol A (DGEBA) with the epoxide value of 0.48–0.54 provided by Wuxi Lanxing Co., Ltd. (China). 4,4′-diaminodiphenylmethane (DDM), which was supplied by China National Medicine Co., Ltd., was chosen as curing agent. The resin and curing agent were mixed at a 100:28 weight ratio and then heated and degassed for 15 min. The above mixture was soaked through the carbon fibre layers under vacuum and cured at 80 °C for 2 h and then 150 °C for 4 h. The content of resin component in the composite sample was 38.5 wt%. Fig. 1 shows the chemical structures of the epoxy resin, curing agent DDM and the matrix of CFRP.

2.2. Decomposition experiments of CFRP

The obtained CFRP sheets were cut into pieces of 1.5 cm × 4 cm. The decomposition reaction was conducted at a designed temperature in 100 mL autoclave without stirring under argon. After cooling, the reaction mixture was filtered and then the solid residue was separated and washed with water, ethyl acetate and acetone for several times. The decomposition products in ethyl acetate phase was evaporated and dried under vacuum. The recovered fibre was dried under vacuum at 70 °C for 12 h.

Table 1
Effects of phenol and KOH on the decomposition efficiency of CFRP.

Entry	Phenol [g]	KOH [g]	Decomposition efficiency [wt%]
1	0	0	12.0
2	5	0	14.5
3	0	0.5	28.0
4	5	0.5	95.2

Reaction conditions: $T = 315$ °C, $t = 30$ min, $V_{H_2O} = 50$ mL, composite mass/H_2O volume (g/mL) = 1/30.

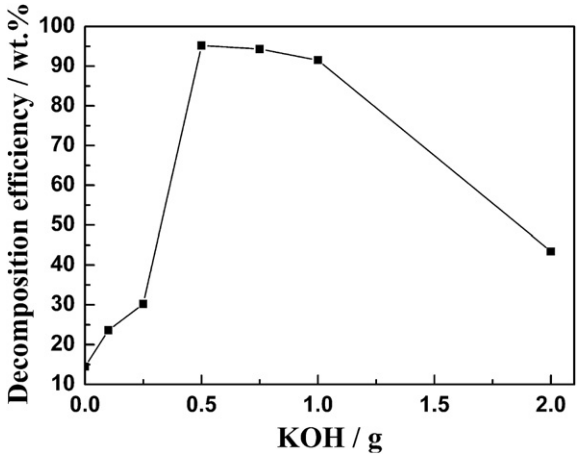


Fig. 2. The amount of KOH against decomposition efficiency. Reaction conditions: $T = 315$ °C, $t = 30$ min, phenol = 5 g, $V_{H_2O} = 50$ mL, $P \approx 9$ MPa, composite mass/H_2O volume (g/mL) = 1/30.

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