Polymer Degradation and Stability 115 (2015) 16–23

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Recycling thermosetting polyester resin into functional polymer using subcritical water

Takaharu Nakagawa [a, b, *], Motonobu Goto [b]

[a] Eco Solutions Company, Panasonic Corporation, 1048 Kadoma, Osaka 571-8686, Japan
[b] Department of Chemical Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

ARTICLE INFO

Article history:
Received 15 September 2014
Received in revised form
23 January 2015
Accepted 3 February 2015
Available online 20 February 2015

Keywords:
Subcritical water
Thermosetting polyester resin
Recycling
Hydrolysis
Styrene-fumaric acid copolymer
Glycol

ABSTRACT

Subcritical water and soluble alkali were applied to hydrolyze thermosetting polyester resins of fiber reinforced plastic (FRP) to recover a styrene-fumaric acid copolymer (SFC) in high yield. SFC is a functional polymer and has the same molecular structure as that of styrene-maleic acid copolymer, which is applied as high value-added additive. Potassium hydroxide (KOH) contributed to accelerate hydrolysis and to provide water solubility to the SFC. The optimized reaction conditions based on the SFC yield were at either a temperature of 230 °C, reaction time of 2 h, and with a KOH concentration of 0.38 mol/L, or 230 °C, 1 h, and 0.72 mol/L for sodium hydroxide (NaOH). It was verified that this method had the potential to recycle thermosetting polyester resin of FRPs to produce SFC.

1. Introduction

Thermosetting polyester resins are generally used in fiber reinforced plastics (FRP) with glass fibers and inorganic fillers. FRP has been applied to various products, such as boats, tanks, and motors. FRP is also widely applied to bathtubs in Japan. Thermosetting resins cannot be re-molded like thermoplastic resins. The high content of inorganic material in FRP creates difficulties in incineration. Therefore, most FRPs have been landfilled. Environmental legislation such as the EU-directives also requires true material recycling of FRP. However, no chemical recycling technology of thermosetting polyester resins into raw materials for resins or other organic compounds has been commercialized.

Chemical recycling of thermosetting polyester resins is worth considering not only for a view point of horizontal recycling into resin raw material, but also for enhancing recycling into functional polymer. Styrene chains form during the curing process of unsaturated polyesters, which have higher value than the resin raw materials. If all ester bonds trapping the styrene chains are hydrolyzed, styrene-fumaric acid copolymer (SFC) should be obtained. The molecular structure of SFC is similar to that of styrene-maleic acid copolymer, which is a functional polymer and is applied as high value-added additives. Moreover, the styrene-maleic acid copolymer could become more expensive due to a lack of benzene according to the demand-supply gap of benzene, the raw material of styrene, which cannot be produced from shale gas. SFC has therefore the potential to replace styrene-maleic acid polymer. Such valuable materials that could be used as raw compounds, additives in new resins, and functional polymers are wastefully landfilled.

There are various strategies for recycling FRP. In the grinding method, mechanically ground FRP is applied as inorganic filler in concrete, cement components, plastic, etc. [1–3]. In the thermolysis method, glass fiber and/or inorganic filler are recovered after pyrolysis or combustion [4–7]. In these approaches, thermosetting resin is not recovered as precursor for new resins.

Various chemical recycling approaches of FRP such as solvolysis have also been studied. Diethyleneglycol monomethylether (DGMM) and benzyl alcohol (BZA) [8], glycol [9–11], amino alcohols, and polyamines [12,13] were investigated. Supercritical methanol was also applied to recover dimethyl phthalate (DMP) [14–18].

Water has also been applied as an agent for chemical recycling of FRP. Superheated steam [19] and subcritical water [20,21] have been used to recover glass fibers. Oliveux et al. used subcritical

* Corresponding author. Tel.: +81 6 6909 1250.
E-mail addresses: nakagawa.takaharu@jp.panasonic.com, takaharu.nakagawa@jp.panasonic.com (T. Nakagawa).

http://dx.doi.org/10.1016/j.polymdegradstab.2015.02.005
0141-3910/

water to recover propylene glycol and phthalic acid [22,23]. Suyama et al. also used subcritical water with an aminoalcohol or hydroxyl compounds having a long alkyl chain and alkylamines to recover polystyrene derivatives [24,25]. We reported that subcritical hydrolysis of thermosetting polyester resin at 360 °C, 18.7 MPa. Only glycols and fumaric acids were recovered [26].

In some of the above chemical recycling approaches, material recycling of the resin was demonstrated. However, all of them are horizontal recycling methods that recover resin raw materials such as glycol and phthalic acid and re-crosslink them with new resin raw materials. There has been no method to recover SFC as a functional polymer from the thermosetting polyester resin waste and apply it to high value-added additives.

In this work, subcritical hydrolysis of unsaturated polyesters using either potassium hydroxide (KOH) or sodium hydroxide (NaOH) as catalysts was investigated. The optimization of the reaction conditions using KOH and NaOH was also conducted. In addition, various real FRPs waste was tested to verify the applicability of this method.

2. Concept of recycling of thermosetting polyester resins using subcritical water

Thermosetting polyester resin is obtained by crosslinking unsaturated polyester (UP) polymer with styrene. The UP consists of glycol and carboxylic acid such as fumaric acid and ortho- or isophthalic acid. Maleic anhydride is used as UP raw material, which isomerizes to fumaric acid during polyesterification. Styrene reacts with the fumaric acid of the UP to form a functional polymer, the styrene-fumaric acid copolymer (SFC). This polymer has a similar molecular structure to that of styrene-maleic acid copolymer which is obtained by hydrolysis of styrene-maleic anhydride copolymer (SMA). Both of these are widely applied as various high value-added additives. However, no approach to extract SFC from the solid thermosetting polyester resin waste to apply it as high value-added additives has been explored.

We have reported that SFC was recovered by subcritical hydrolysis of the thermosetting polyester resin [27–29]. Subcritical water is well known to have significant reactivity due to its higher ion product than normal water and to its low dielectric constant equivalent to that of organic solvent [30]. Therefore, it has an advantage over other chemical recycling approaches in terms of breaking ester bonds more effectively. We have successfully demonstrated that most of ester bonds of the thermosetting polyester resin were hydrolyzed efficiently using subcritical water with KOH to recover SFC in high yield [27–29]. The SFC modified with benzyl chloride showed almost equivalent shrinkage control effect as a commercial low profile additive (LPA), which is a high value-added additive used in FRPs to control the shrinkage. Then, the possibility of recycling thermosetting polyester resin into higher value products than resin raw materials was verified. It is from 5 to 10 times more expensive than styrene monomer.

The alkali salt of the styrene-maleic acid copolymer has been applied to various high value-added additives such as emulsion polymerization, overprint varnish, inks, textile/leather treatment, carpet cleaners, polymer modification, and adhesives. In subcritical water hydrolysis with alkali, a reaction slurry containing solid residue is obtained after the reaction. The reaction slurry is separated by filter press into reaction liquid and solid residue including milled glass fibers, inorganic fillers, and unreacted resin. The reaction liquid contains the alkali salt of the SFC, which can be directly applied to the same applications as the alkali salt of styrene-maleic acid copolymer.

Fig. 1 shows the concept of chemical recycling of the thermosetting polyester resin using subcritical water. After crosslinking of the UP by styrene, a lattice structure with the styrene chains is constructed. The subcritical water hydrolysis with KOH was optimized to avoid thermal degradation of the styrene chains and to make hydrolysis the dominant process. The potassium salt of SFC dissolved into the aqueous solution and was obtained with high yield after hydrolysis at 230 °C, 2.8 MPa during 4 h. The SFC recovered after acidification of its potassium salt showed a weight-average molecular weight (Mw) of 30,000 and a styrene/fumaric acid (S/F) molar ratio of 2.2. While exploring an application for the SFC, we focused on a low profile additive (LPA) for the FRP forming process since its molecular structure was similar to that of the LPA usually used. The SFC was modified with benzyl chloride to develop shrinkage control performance. A recycled LPA using the modified SFC successfully exhibited a shrinkage control effect equivalent to a commercial LPA [27–29].

In subcritical water hydrolysis of FRP, the soluble alkali such as KOH, is suggested to play a very important role to realize an ideal reaction and high yield of the SFC. The optimization of reaction conditions and alkali is necessary for industrialization.

3. Material and methods

3.1. Subcritical hydrolysis of thermosetting polyester resins

Thermosetting polyester resin sample was prepared according to the composition given in Table 1. The UP was prepared with glycols and maleic anhydride. The UP resin is viscous liquid consisting of styrene and the UP. The UP resin and calcium carbonate ($CaCO_3$) were mixed together and cured at 100 °C for 2 h to produce thermosetting polyester resin sample. The obtained material was then heated to release unreacted styrene monomers after curing. Hydrolysis was also realized on uncured polyester, from which styrene was evaporated by heating.

Samples of the material were placed into a 20 mL batch tubular reactor. Pure water or KOH aqueous solution (0.2–1.0 mL/L) was

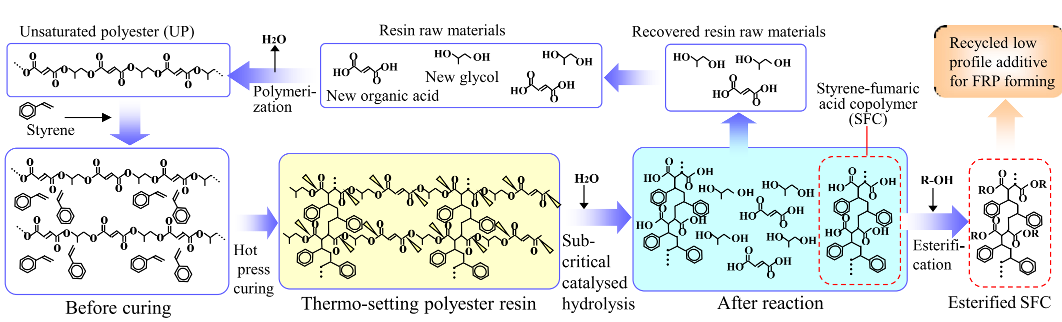

Fig. 1. Concept of the recycling of thermosetting polyester resins recycling using subcritical water.