SYNTHESIS OF UNSATURATED POLYESTER RESIN FROM GLYCOLYSED POSTCONSUMER PET WASTES

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Abstract

In this work the production of secondary value-added products, such as unsaturated polyester resins (UPE), derived from the chemical recycling of polyethylene terephthalate (PET) was examined. Glycolysis of PET waste granules was carried out using excess ethylene glycol in the presence of sodium carbonate as catalyst. High yields (80%) of the monomer bis(2-hydroxyethyl terephthalate) were obtained. This recovered monomer was polyesterified with maleic anhydride to form unsaturated polyester resins. Upon addition of styrene monomer, UPEs were casted by crosslinking reaction using methyl ethyl ketone peroxide and cobalt octoate as initiator and catalyst, respectively. The polyesterification reaction was followed by GPC and the cured resin was subjected to various characterization techniques in order to determine its chemical, physical and mechanical properties.

Keywords: *PET wastes, recycling, glycolysis, unsaturated polyester resin, bis(2-hydroxyethyl) terephthalate*

1. Introduction

Poly(ethylene terephthalate) (PET), a semi-crystalline thermoplastic polyester that is extensively used in diverse applications -textiles, high strength fibers, photographic films, disposable soft-drink bottles, and others- is also one of the largest components of the post-consumer plastics in landfills.

The principle of chemical recycling is to convert high molecular weight polymers into low molecular weight substances via chemical reaction. PET can be depolymerized into monomer or low molecular weight oligomers via glycolysis reaction in excess ethylene glycol [1,2]. Further, the monomer, bis(hydroxyethyl) terephthalate (BHET) thus obtained can be used as building blocks to synthesize other polymers with higher economical values such as unsaturated polyesters, polyurethane foams, polyisocyanurate foams, copolyesters, polyurethane coatings, alkyd resins, low temperature curable resins, or UV curable resins [3,4].

The purpose of this research is to develop a new method of producing unsaturated polyester resins (UPR) from the BHET obtained via glycolysis of PET wastes.

2. Materials and Methods

Glycolysis of PET waste granules was carried out using excess ethylene glycol in the presence of zinc acetate and sodium carbonate acting as catalysts. Experiments were carried out in a batch reactor at atmospheric pressure. After a specified time interval the product (BHET) was separated through two consecutive steps (extraction with hot water followed by crystallization). The BHET was quantified by gel permeation chromatography (GPC) and subjected to various characterization techniques, namely elemental analysis (EA), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR).

UPR was prepared by the polyesterification reaction of the recovered BHET with maleic anhydride. Synthesis was carried out in a round-bottom flask connected to a distillation condenser. Afterwards, unsaturated resin was mixed with styrene 35% weight and hydroquinone was also added in order to inhibit initiation of the polymerization. In order to cure the resin, methyl ethyl ketone peroxide (MEKP) and cobalt octoate were used, as initiator and catalyst, respectively, at a weight ratio of 100:0.5:0.5.

The polyesterification reaction was followed by GPC and the cured resin was subjected to various characterization techniques: differential scanning calorimetry, Fourier transform infrared spectroscopy, flexural dynamic mechanical thermal analysis (DMTA) and thermogravimetric analysis (TGA). Curing behaviors (curing time and temperature) were also analyzed.

3. Results and Discussion

Glycolysis of PET wastes

The effect of various operation parameters on the catalysed glycolysis of PET waste was investigated in order to efficiently recover its purified monomer. The yield of monomer increased with an increase in EG:PET

molar ratio, temperature, amount of catalyst and reaction time until the reaction reached equilibrium conditions [1]. Hence, a yield of high purity BHET close to 80% could be attained at 196 ºC, with an EG:PET molar ratio of 7.6:1 and using zinc acetate as catalyst with a concentration (PET:catalyst molar ratio) of 380:1.

In an attempt to find an alternative to zinc acetate, a highly active catalyst for the process but with a considerable environmental impact, several eco-friendly simple salts were examined namely, sodium carbonate, sodium bicarbonate, sodium sulphate and potassium sulphate. From the comparison of the efficiencies it was found that sodium carbonate could depolymerize PET wastes almost as efficiently as zinc acetate does at the cost of using a slightly higher concentration in the reaction mixture. The environmental impact of the glycolysis process can be markedly diminished since the use of Zn cation (commonly used) is avoided.

The purity of the recovered BHET after PET waste glycolysis, was determined by means of a number of analytical techniques, and the results were compared with those corresponding to a commercial BHET sample provided by the Aldrich Chemical Co. From all these observations it was concluded that the product from glycolysis was highly pure BHET.

Synthesis of unsaturated polyester resins

The effect of various operation conditions on the UPR synthesis was investigated. The molecular weight of the resin increased with reaction time and temperature as showed by GPC analysis (Fig. 1).

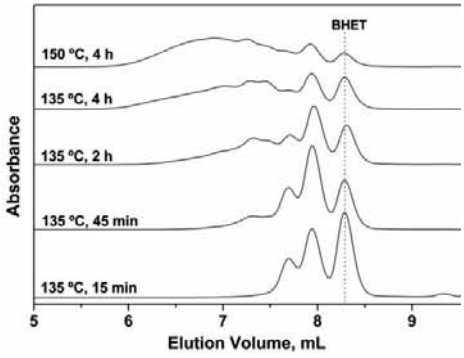

Fig. 1. UPEs GPC chromatographs.

Firstly, the amount of hydroquinone used for inhibiting undesired polymerization was optimized. The same resin varying amounts of hydroquinone (0.05-0.045% wt) was cured with MEKP and cobalt octoate as initiator and catalyst respectively, and then was analyzed by DMTA. A sinusoidal load was applied to the sample and the real (E´) and imaginary (E´´) module were measured. The ratio E´´/E´ is defined as the loss tangent or the damping (tanδ). The tanδ peak temperature was taken as the glass transition temperature (T_g). The tanδ and T_g decreased when the amount of hydroquinone increased. Thus, the resin obtained with higher amounts of inhibitor presented inferior thermal properties. 0.02% wt was chosen as the optimal amount.

After optimizing the curing conditions, UPE synthesized under different conditions were compared. Glass transition temperature (T_g) of cured UPE resins was analyzed from DSC thermograms. It was observed that T_g increased with an increase in the reaction time and temperature. As example, T_g(4h, 150 ºC)= 55 ºC, T_g(6h, 150 ºC)= 63 ºC, T_g(8h, 135 ºC)= 77 ºC and T_g(8h, 150 ºC)= 82 ºC. T_g of the prepared resin varied from 50 to 85 ºC. This range of temperature for the glass transition was within the range expected for a fully cured UPR [5].

FTIR spectra were recovered for all synthesized resins. All of them showed the same spectra. The absorption at 3400, 3000-2800, 1750 and 1300 cm^{-1} corresponded to OH, C-H, C=O and C-O stretching, respectively. A sharp peak around 750 cm^{-1} was related to the para-sustituted aromatic ring, which is characteristic of PET [4].

4. Conclusions

Recycling of PET waste through glycolysis was successfully performed, cracking the polyester into monomer. Polyesterification of the monomer with maleic anhydride was completed to obtain an unsaturated polyester resin. The unsaturated resin was cured with MEKP and cobalt octoate, and analyzed with various characterization techniques.

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