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Curable resins based on recycled poly(ethylene terephthalate) for coating applications

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Abstract

Poly(ethylene terephthalate) waste was depolymerised in the presence of diethylene- or tetraethylene glycol and manganese acetate as a catalyst. An epoxy resin was then prepared by the reaction of these oligomers with epichlorohydrin in presence of NaOH as a catalyst. The produced oligomers were condensed with maleic anhydride and ethylene glycol to produce unsaturated polyester. The chemical structures of the resulting epoxy and unsaturated polyester resins were confirmed by ^{1}HNMR. The vinyl ester resins were used as cross-linking agents for unsaturated polyester resin diluted with styrene, using free radical initiator and accelerator. The 2-amino ethyl piprazine was used as hardener for epoxy resins. The curing behaviour of the unsaturated polyester resin, vinyl ester resins and styrene was evaluated at different temperatures ranged from 25 to 55 °C to calculate the curing activation energy of the system. The cured epoxy and unsaturated polyester resins were evaluated in coating application of steel.

Keywords: Unsaturated polyesters; Poly(ethylene terephthalate); Recycling; Epoxy resins; Curing behaviours

1. Introduction

Recycling techniques, such as reprocessing with virgin resin, blending and pyrolysis of waste plastics, recycling through solutions and chemical reactions, are effective routes to alleviate environmental pollution produced from plastic wastes [1–3]. Poly(ethylene terephthalate), PET, is one of the most important recycled polymers. PET is increasingly conventional material such as paper, wood, metal and glass in a variety of volume applications. PET is used widely for many applications such as fibers, films, sheets and soft drink bottles. PET accounts for 8% by weight and 12% by volume of the world's solid waste [4]. PET waste is typically found in scrap textiles and in beverage bottles. However, these very properties make PET a non-biodegradable material resulting in a solid waste disposal problem. Chemical recycling of PET, which includes methanolysis, hydrolysis, glycolysis, aminolysis, ammonolysis, and degradation, or cracking, provides a very potent way to recover raw materials, such as terephthalic acid and ethylene glycol or oligomer, and some other useful small molecules [5,6].

Nowadays, the major producer of PET is concentrating on the manufacturing processes, which minimize the generation of solid waste as well as reclamation, recycling or disposal of such material by environmentally appropriate means [3]. Previous investigations [7–11] studied the production of curable resins from recycled PET. The recycling of PET to form curable resins would also help to alleviate an environmental problem. The first aim of the present study was to prepare epoxy, unsaturated polyester and vinyl ester resins from depolymerised oligomers of PET using tetraethyleneglycol (TEG) and diethylene glycol, DEG, to produce curable resins. Secondly, the blending of the prepared unsaturated polyester with vinyl ester resins in order to influence their curing behaviour and mechanical properties is another goal. In this respect TEG was selected to modify the chemical structure of the vinyl ester resin and to prepare a more flexible resin. Finally, the prepared resins were evaluated in coating applications of steel.

2. Experimental

2.1. Materials

PET waste was collected from beverage bottles. It was crushed to small pieces after washing with soap and methanol

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and removing of adhesive materials. The intrinsic viscosity of PET in m-chlorophenol at 25 °C was found to be 0.015 $dm^3\,kg^{-1}$. The weight average molecular weight was determined by gel permeation chromatography (GPC) to be close to 63,200 $g\,mol^{-1}$. Tetraethyleneglycol (TEG) and diethylene glycol (DEG) were used as supplied. Epichlorohydrin (EC) was used after distillation. Manganese acetate was used as the transesterification catalyst for the depolymerization of PET. Acrylic acid (AA) and methacrylic acid (MA) were used without further purification. Methyl ethyl ketone peroxide (MEKP) and cobalt octoate (Co) were used as initiator and accelerator, respectively. MEKP was supplied as a 50% paste in dimethyl phthalate. The Co was a 10% solution in styrene. 1-(2-Amino ethyl) piprazine (AEP was used as hardener. High purity acetone, toluene and pyridine were used as received. All chemicals were supplied by the Aldrich chemical company.

2.2. Techniques

2.2.1. Synthesis of epoxy and unsaturated polyester resins from recycled PET

PET waste (0.454 mol) was depolymerized with TEG (0.575 mol) or DEG (0.943 mol) in the presence of 0.5% (by weight) of manganese acetate based on the weight of PET in a nitrogen atmosphere at 200 °C for 4 h, and then at 210–230 °C for 3 h. The produced oligomers were purified as described in previous publication [11]. The purified oligomers with residual TEG or DEG were analysed to determine the hydroxyl value by the conventional acetic anhydride/pyridine method [12]. The purified oligomer of glycolised PET waste with TEG and DEG were abbreviated here as GT and GD, respectively.

Synthesis of epoxy resins and vinyl ester resins from recycled PET oligomers was reported in previous article [7]. The glycidyl ethers of the glycolysed PET with TEG and DEG were designed as GTE and GDE, respectively. They were obtained as a viscous liquid and the epoxy content was determined by a previously reported method [13]. The diacrylate and dimethacrylate oligomers produced from GTE were designated here as GTA and GTM, respectively. The chemical structures of GTA and GTM were analysed by ^{1}HNMR.

UP was prepared from GD oligomer using MA and EG as described in previous method [8].

2.2.2. Physical measurements

The prepared UP was dissolved in $CDCl_3$ and analysed using a Jeol ^{1}HNMR spectrometer model JNM-EX (270 MHz) to determine their chemical structures. Their molecular weights were measured using a GPC (Water Model 600 E).

The curing exotherms of the unsaturated polyester UP were measured in the presence of GTA and GTM, using MEKP as initiator and Co as accelerator, as described in previous work [7]. The UP was dissolved in 40% (w/w) of styrene monomer and mixed with various weight percentages of GTA and GTM (0–20%). The curing exotherms were determined at different temperatures ranged from 25 to −65 °C. The concentrations of MEKP and Co were 2% and 0.2% (w/w) with respect to the total weight of the cured samples [7].

The gel times of the cured unsaturated polyester in the presence of styrene and vinyl ester resins were determined by measuring the change in the viscosity of the mixture as a function of time at constant temperature and shear rate. The viscosity measurements were determined by using a Brookfield Model Dv-111 programmable Rheometer.

The critical value for the viscosity (η_c) and time (t_c) corresponding to the gel point were determined from the relation between the initial viscosity of the resins and the curing time. This procedure was repeated at different temperature intervals ranged from 25 to 55 °C.

2.2.3. Testing of the coatings

It is common to use mild steel panels (15 cm × l0 cm) to evaluate the different properties of coatings. The other side of panels is coated and protected against corrosion environments by using coal tar epoxy primer. The tested side was blasted and cleaned to apply the coated materials. Then the panels are subjected to different testing procedure to evaluate their mechanical properties and their durability. Adhesion strength, mechanical properties (pencil hardness, impact, *T*-bend tests), chemical resistances (hot water, acid and alkali resistance, salt spray resistance and solvent resistance) were measured according to ASTM methods as reported in a previous study [14].

The acid and alkali resistances of coated panels were determined after immersion in 10% of HCl and 5% of NaOH aqueous solutions using distilled water. The duration of the test was 90 days at 38 °C. The degree of adhesion and visual inspection of blister and cracks were evaluated for the coated panels.

3. Results and discussion

Using the recycled PET offers the possibility of a lower cost source for production of curable resins. The present study is intended to prepare epoxy, UP and vinyl ester resins from recycled PET waste to use in coating applications. Tong et al. [15] found that unsaturated polyesters based on bis(2-hydroxyethyl) terephthalate, maleic anhydride and ethylene glycol were not compatible with styrene monomer. It was found that, the replacement of the ethylene glycol by another type of glycol enhances the compatibility of the products with styrene monomer. In the present study TEG was incorporated in the vinyl ester to increase the miscibility of the synthesized resins with styrene monomers. Schulze et al. [16] have reported on the modification of unsaturated polyesters by poly(ethylene glycol) end groups in order to modify its solution behavior in styrene and to modify the mechanical properties of the cured resin. It was found that, the conversion of the typical polar end groups to poly(ethylene glycol) end groups improved the flexibility of the cured material. Accordingly we presumed that the incorporation of TEG into the structure of the vinyl esters will enhances their solubility in styrene monomer. On the other hand, DEG and TEG were used to modify the chemical structure of the prepared epoxy and UP resins to modify both mechanical and chemical resistances of cured resins.