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Synthesis of Unsaturated Polyester Resin Based on Pet Waste

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Abstract: Polyethylene terephthalate (PET) flakes are widely used as raw material for manufacturing of packaging materials. The worldwide production of PET is 30.5 million metric tons/year. With such a large consumption, the effective application of PET waste is of considerable commercial and technological significance. In this paper we used PET flakes for the synthesis of unsaturated polyester resin to go green. PET flakes were depolymerized by using Neopentyl glycol (NPG) and propylene glycol (PG). Glycolized product was reacted with maleic anhydride and phthalic anhydride. Then it was mixed with styrene monomer to get unsaturated polyester (UP) resins. Molecular weight, Hydroxyl value and Acid value of all synthesized UP resins were studied.

Keywords: Polyethylene Terephthalate, depolymerization, glycolysis, Unsaturated Polyester resin, Sustainable.

I. INTRODUCTION

Unsaturated polyester (UP) resins are widely used reinforced plastics due to their low cost and versatility. An unsaturated polyester resin (UP resin) is a solution of the unsaturated polyester in a low-viscosity monomer, which also contains carbon-carbon double bonds. [1] The most common monomer used is styrene. The carbon - carbon double bonds in the UP can react with the carbon-carbon double bonds in the monomer by means of a radical-initiated polymerisation reaction. This process is called curing or cross-linking. The result is a three-dimensional (cross-linked) network. [2] The product becomes a solid material, which no longer (contrary to thermoplastic polymers) melts during heating UP resins can meet specific requirements by proper choice of chemical building blocks. The most commonly used diols are ethylene glycol (EG), propylene glycol (PG) and neopentyl glycol (NPG) whereas the diacids include phthalic anhydride, isophthalic acid, adipic acid, maleic anhydride and fumaric acid. Each of these materials can affect final properties of the products.

For instance, the general purpose (GP) resin is prepared by polycondensation of PG, maleic anhydride and phthalic anhydride. Terephthalic acid is used instead of phthalic anhydride certain properties such as heat distortion temperature (HDT) and chemical resistance are improved. Hence, UP resins which have terephthalate base in their structures are one of the most useful and versatile polyester resins; however, the direct use of TPA in synthesis of UPR is difficult because of its high melting point and processing difficulties arising from its sublimation during the reaction. Thus, formulations involving terephthalic acid are more expensive, whereas UP resins prepared by glycolized poly(ethylene terephthalate) (PET) waste offer some economic advantages. Furthermore, synthesis of UPR from recycled PET can alleviate environment pollution. Therefore, the concept of preparing unsaturated polyester resin from the glycolized PET products is well developed.[3] The glycolysis of PET with glycols in the presence of zinc acetate yields terephthalic oligomers by transesterification. After that the oligoester diols react with maleic anhydride and other dibasic acids to form UPR. Due to the importance of the above-mentioned reactions, many studies have been determined on glycolysis of PET wastes. Different important factors such as reaction conditions (temperature, pressure, glycolysis time), kind of glycol and reactants ratio were investigated.[4] The activation energy for the uncatalyzed glycolysis is about 32 kcal/mol, whereas a proper catalysed process requires less than 20 kcal/mol.[5] Thus, various metal-containing catalysts, such as zinc acetate[6], lead-, cobalt- or manganese acetate [7] and titanium alkoxides [8] or other titanium compounds [9] such as titanium (IV)-phosphate compound were used to facilitate the process. The most effective catalyst is zinc acetate compared to other ones. Although the reaction proceeds faster in the presence of titanium alkoxides compared with the depolymerization catalysed by metal acetate compounds, side-reactions proceed faster that yield products with an undesirable yellowish colour. Zinc acetate is more used compared to titanium alkoxides for glycolysis reaction of PET. In this study, it is observed that the role of a co-catalytic system in glycolysis reaction of PET and UPR synthesis. Hence, the effect of cyclohexylamine as the co-catalyst on the glycolysis reaction in the presence of zinc acetate (the major catalyst) was evaluated and an optimum amount of cyclohexylamine was found. Finally, UP resins were synthesized by reaction of glycolized products with anhydrides and the effect of the co-catalytic system on UPR synthesis was studied.[10]

The cross-linking reaction is a radical-initiated polymerisation reaction. Organic peroxides are used as radical initiators. [11] There are many ways to process UP resins and each process has its own most appropriate organic peroxide. Radicals are generated by the decomposition of the organic peroxide. This is caused either by heat or accelerators. The latter are frequently solutions of metal salts such as cobalt octoate with a concentration between 1 and 10% Co as the metal. [12]

By adding organic peroxide and the cobalt salt solution we get curing reaction of UP resins at room temperature. Care must always be taken not to mix the peroxide and the cobalt solution in a pure form, as this will result in a violent decomposition reaction. [13] The polyester resin is premixed with cobalt in the resin, so the reaction can be started by just adding the proper amount of organic peroxide. Methyl ethyl ketone peroxide (MEKP) is the organic peroxide that is most-used one for cold curing processes. [14] When both the components are added, radicals form which react with the carbon- carbon double bonds to form reactive places on the molecule. Polymer chains take time to cross link with the styrene molecules. The product obtained is in liquid state. As soon as the cross-linking reaction has progressed sufficiently, the resin forms a gel under the generation of heat. [15] The choice of the curing system determines the speed of the reaction and the gel time. [16] After gelation, the resin cannot be processed anymore. [17]

II. EXPERIMENTAL

A. Materials

Post-consumer PET bottles supplied by Das enterprise and were crushed to small pieces after washing with acetone and methanol to remove adhesive and other materials. The intrinsic viscosity of PET in 58:42 (w/w) phenol/1,1,2,2-tetrachloroethane solution at 25°C was about 0.770 dl/g, corresponding to a number-average molecular weight of 3.42×10^4 g/mol. Propylene glycol and Malic Anhydride were purchased from Yashochem and zinc acetate were obtained from Thomas Bakers. Phthalic Anhydride purchased from BMG chemicals. NPG supplied by Nandlal & Sons.

B. Glycolysis of PET Waste

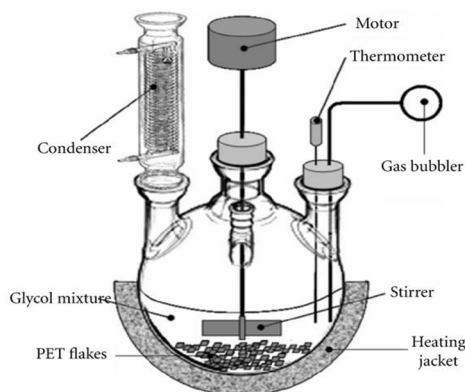


Figure 1 : Glycolysis of PET

The PET waste was depolymerized with Neopentyl glycol using 0.5% (w/w) zinc acetate, based on PET weight, as the major catalyst. The reaction was carried out at about 210°C under reflux and nitrogen blanket and the weight ratio of PET to NPG was 2:1. The reactor was a four-necked, round-bottomed flask of 3 Liter capacity having a reflux condenser, thermometer and stirrer. The glycolysis of PET waste was carried out in six different reaction times, 5 to 9 hr at 1-hr intervals, with and without cyclohexylamine to investigate the progress of reactions in the presence of each kind of catalytic system.

Table 1: Formulation for UPR

Materials	Quantity
PET FLAKES	43.54
NPG	28.35
MALIC ANHYDRIDE	11.11
PHTHALIC ANHYDRIDE	17.00
TOTAL	100.00

III. RESULTS AND DISCUSSION

A. Determination of Hydroxyl Value

The hydroxyl values were determined by using acetic anhydride/pyridine reagents. 2g of the sample was weight into the flask. Pipet 5ml of the pyridine - acetic anhydride reagent into the flask containing the sample for acetylation. Pipet 5ml of pyridine - acetic anhydride reagent into an empty flask for the reagent blank. Place the flask on a steam bath, under a reflux condenser and heat for 1hour. Add 10ml of water through the condenser to the flask and heat on the steam bath for an additional 10min with the reflux condenser attached. Let the flask to cool down to room temperature with condenser attached. 25ml of butyl alcohol neutralized to phenolphthalein, wash down the condenser with about 12ml, remove the condenser and use the remaining butyl alcohol to wash down the sides of the flask. Add 1ml of phenolphthalein indicator solution. Titrate to a faint pink endpoint with 0.5N alcoholic KOH solution. With this method the hydroxyl value obtained was in the range of 70-80.

$$\text{Hydroxyl Value} = \frac{(B + \frac{WA}{C}) - S}{W} \times N \times 56.1$$

Where,

A= mL KOH solution required for the acidity titration.

B= mL KOH solution required for, the reagent blank.

C= weight of sample used for the acidity titration.

S= mL KOH solution required for titration of the acetylated sample.

W= weight of sample used for acetylation

B. Determination of Acid value

The acid value was determined by titrating the solution of the weighed quantity of resin in acetone, with about 0.1 N KOH solution using pink phenolphthalein indicator. The final acid value obtained was in the range of 25-30.

$$\text{Acid value} = \frac{56.1 \times N_{\text{KOH}} \times B}{W}$$

Where, B = mL KOH solution required

W = weight of sample

C. Determination of Viscosity

The determination of viscosity was done in Gardner tube. The viscosity of UPR resin is checked at 30 °C temperature with solvent keeping the solid content at 60%.

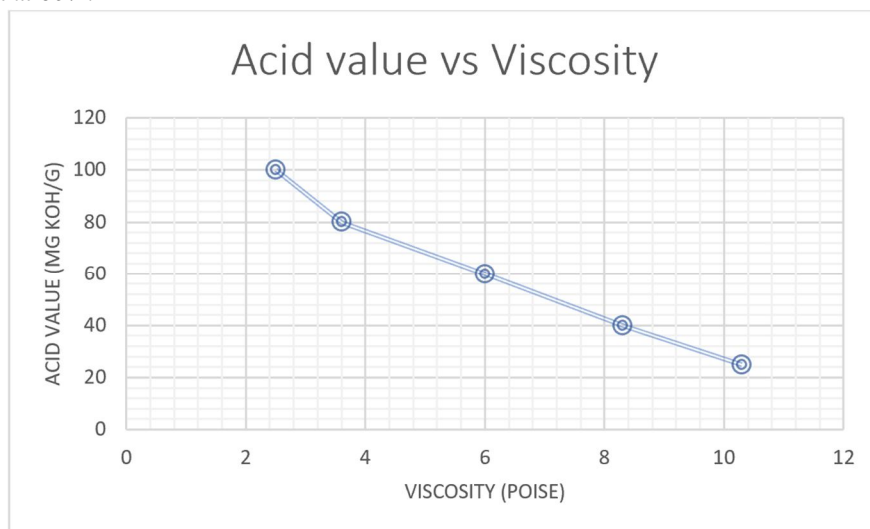


Figure 2: Acid value vs Viscosity

From figure 2, we get to know as the Acid value decreases the viscosity of UPR increases. At 60 % solid, the viscosity is 10.3 poise when the Acid value is 25. It is then further reacted with styrene monomer at controlled temperature. Then for further application it is mixed with MEKP.

IV. CONCLUSION

The PET-based unsaturated polyester resins were prepared by reacting the glycolysis products of waste PET with maleic anhydride, phthalic anhydride, and NPG glycol at the same OH/COOH molar ratio, with the waste PET based resins. The Hydroxyl value of UPR obtained was 70-80 . At 60 % solid, the viscosity is 10.3 poise and Acid value is 25. It is then further reacted with styrene monomer at controlled temperature. Then for further application it is mixed with MEKP.

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