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Kinetics study of Unsaturated Polyester synthesized from waste PET

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ABSTRACT: Waste polyethylene terephthalate (PET) is glycolyzed along with virgin PET. A higher proportion of virgin PET in the mixture has the ability to consume more glycols during glycolysis. This gives rise to a glycolyzed PET (GPET1), which contains a lesser amount of free glycol and shows the highest hydroxyl value. During polyesterification of the polyester diol (glycolyzed PET) with maleic acid, the degree of polymerization (DPn), extent of reaction and acid value is observed to be increasing with an increase in the virgin PET content in the mixture. This is believed to be due to the increasing presence of BHET (bis-hydroxy ethylene terephthalate) in the glycolyzed PET.

Keywords: Glycolyzed PET; BHET; polyesterification; hydroxyl value.

INTRODUCTION

Polyethylene terephthalate (PET) is one of the most versatile plastics, which are widely used in the manufacturing of various kinds of packaging, especially for soft drink bottles, fibers and films. The overall annual world consumption of PET amounts to about 13 million tons (Mansour and Ikladious, 2002). Although several methods have been proposed for recycling waste PET, it is suggested that the most attractive method is chemical glycolysis into corresponding monomers or raw chemicals. These glycolyzed products could be reused for the production of plastics or other advance materials (Suh et al., 2000). The aim of most of the chemical recycling procedures is obtaining monomers, such as terephthalic acid (TPA), ethylene glycol (EG) and bis(2-hydroxyethyl) terepthalate (BHET). The first two can be obtained by hydrolysis under neutral, acidic or alkaline conditions and the last one by glycolysis of the waste PET.

An excellent review summarizes the research and application up to 1997 (Paszum and Spychaj, 1997). Some recent additions are papers on alkaline (Wan et al., 2001 and Kao et al., 1998 and Karayannidis et al., 2002) and acidic (Yoshioka et al., 2001) hydrolysis and glycolysis (Guclu et al., 1998 and Chen 2001) and patents on glycolysis (Ekart and Pell, 1997 and Peterson, 2000, Ekart and Murdoch, 2002). In a recent study, Vaidya and Nadkarni (1987, 1989) suggested the synthesis of unsaturated polyester (UP) resin from PET waste and also investigated the kinetics of glycolysis on several glycols. Baliga and Wong (1989) carried out the glycolysis of PET with ethylene glycol (EG), using various metal-acetate catalysts. They found that glycolyzed products had 1-3 repeating units depending on the catalyst used. Numerous researchers (Rebeiz et al., 1995 and Rebeiz, 1994) tried to apply this unsaturated polyester to polymer concrete by replacing Portland cement as a concrete binder. Aslan et al, (1997) compared the composite sheet containing unsaturated polyester developed from the recycled PET to the analogous composite made of virgin unsaturated polyester resin. The present paper also reports the synthesis of unsaturated polyester (UP) resins from the glycolyzed PET and their characterization.

MATERIAL AND METHODS

1. Materials used: Discarded PET bottles from soft drinks were procured from scrapers and cleaned thoroughly. The cleaned bottles were further depolymerized. Virgin PET (G 5761, bottle grade), with intrinsic viscosity of 0.76 and crystallinity >50% was obtained from Reliance Industries Ltd., Bombay. Zinc acetate, minimum assay 99%, and ethylene glycol were procured from E. Merck (India) Pvt. Ltd, Bombay.

2. Cutting and Shredding of Waste PET: First of all, PET bottles being used for the carbonated drinks were collected from different sources. These PET bottles were cut into very small pieces with the help of scissors. The size of the flakes was kept around 0.5 cm × 0.5 cm. Some flakes of a size greater than this were also taken to observe the effect of the size on the solubility of the flakes. It was seen that the flakes that were of smaller size dissolved quickly into ethylene glycol as compared to the flakes with comparatively larger sizes.

3. Glycolysis: The used PET scrap was a solid material having its melting point at around 260 ± 2 ºC. The high melting temperature of waste PET requires it to digest with glycol at high temperature. As anaerobic glycolysis was employed, to avoid the side reactions like oxidation at high temperature, virgin PET (bottle grade) was taken in different proportions (see Table 1) along with waste PET. In the presence of ethylene glycol, the melting of PET waste started at around 200 °C and took 9 hours to complete the glycolysis process. The glycolysis was carried out with excess ethylene glycol in the presence of zinc acetate as catalyst under anaerobic conditions and normal pressure. The glycolyzed product on depolymerization for about 8 to 10 hours was light brown in color and its viscosity increased with the decrease in ethylene glycol content.

Table 1: Ratios of virgin and waste PET used and hydroxyl value

S.NO.	Glycolyzed product	Virgin PET/Waste PET (%)	Before free glycol removal	
			Wt% free glycol	Hydroxyl value (mg/KOH)
1	GPET1	90/10	36	1323
2	GPET2	75/25	44	714
3	GPET3	65/35	52	704
4	GPET4	50/50	54	700

3.1 Recovery of BHET (bis-hydroxy ethylene terephthalate): The bulk of glycolyzed product left out was then agitated with cold distilled water to dissolve the unreacted excess ethylene glycol and filtered. The residue left over was then treated with boiling water and filtered. The filtrate on cooling in an ice bath for a few hour yielded white crystalline flakes of bis-hydroxy ethylene terephthalate. Quantitative analysis was done for both the BHET and free ethylene glycol that had been obtained by the depolymerization of PET waste from soft drink bottles and the virgin PET by glycolysis.

4. Analysis of glycolyzed PET:

4.1 Determination of free glycol: The weighed quantity of the glycolyzed product was extracted with water and filtered. The filtrate containing water, free glycol and some oligomers was concentrated by evaporation of water and then distilled in order to precipitate out the water-soluble oligomers. This was filtered again. The precipitates of the first filtrate were formed under chilling conditions, which were then filtered. Both the residues of the sample obtained during filtration as well as the second were weighed together after drying. The difference between the original and the final weight represents the amount of free glycol removed by water extraction.

4.2 Determination of free hydroxyl: About 2 gm of the sample was put in a 250 ml conical flask and the acetylating reagent (acetic anhydride in pyridine) measuring 22.5 ml with the help of the pipette was added. The flask was then put on a water bath (boiling) under reflux for about 3 hours to complete acetylation. The excess of unchanged acetic anhydride was hydrolyzed by adding 15 ml of distilled water and the heating was continued for further 15 minutes. The flask was again rinsed with 15 ml of distilled water. The total free acetic acid was titrated with standard NaOH solution using phenolphthalein as indicator. Similarly, the duplicate experiment was performed without using the glycolyzed product sample (blank titration).

5. Preparation of unsaturated polyesters: Unsaturated polyesters were prepared by the reaction of the glycolyzed product of PET with maleic anhydride at a fixed ratio of hydroxyl to carboxyl group of 1.1:1. The hydroxyl value of the glycolyzed product after separation of free glycol was used to determine the required amount of maleic anhydride. Thus, four unsaturated polyester resins (UP1, UP2, UP3 and UP4) were synthesized by reacting maleic anhydride with GPET1, GPET2, GPET3 and GPET4. The reactants were distilled in a round bottom flask to a temperature of about 160—180 ^oC for 75 min. The liberated water was also measured during distillation. The samples were taken out at different time intervals to study the polymerization kinetics. The polymerization kinetic was studied through the measurement of acid value and the extent of reaction at different time intervals.

5.1 Measurement of acid value of the unsaturated polyester: The same procedure, which is adopted for the measurement of acid of value of the glycolyzed product, was followed. The detailed acid values of unsaturated polyester resins are reported in Table 2.

Table 2: Acid values (gm equivalents) for the different unsaturated polyester resins

Time (in min)	**UP1**	**UP2**	**UP3**	**UP4**
0	2.65	3.16	3.56	3.26
15	1.74	2.55	2.55	1.81
30	1.33	1.21	1.35	1.16
45	0.82	0.92	1.01	1.02
60	0.29	0.75	0.83	0.82
75	0.28	0.66	0.81	0.71

5.2 Measurement of extent of reaction and degree of polymerization: The extent of the reaction (p) and average degree of polymerization (DPn) are represented as (Katoch et al 2009).

RESULTS AND DISCUSSION

The content of the free glycol and the hydroxyl value (mg KOH/gm) of the glycolyzed PET are listed in Table 1. The glycolyzed PET (GPET1), which is obtained from the mixture with the highest proportion of virgin PET, contains the lowest amount of free glycol and exhibits the highest hydroxyl value. On the other hand, the highest free glycol content and the lowest hydroxyl value are observed in the glycolyzed PET (GPET4) obtained from the lowest proportion of virgin PET in the mixture. Among the four mixtures, hydroxyl value is much higher for GPET1 compared to the others. This is probably due to its higher extent of glycolysis, leading to the maximum proportion of BHET. The acid value of all unsaturated acids is reported in Table 2 at different time intervals and is plotted in Figure 1. For all samples, acid value of the reactants decreases with an increase in time. With the progress of time, the acid groups of maleic acid are consumed by glycols, leading to the formation of polyester and thus decreasing the acid value. It is observed that after sufficient time period, UP1 shows minimum acid value whereas UP4 shows the highest acid value. This is due to the reason that UP1 is prepared from GPET1, a glycolyzed PET consisting largely of BHET (small chain glycols like BHET are more reactive than large chain glycols such as oligomers of BHET used for preparation of UP4).

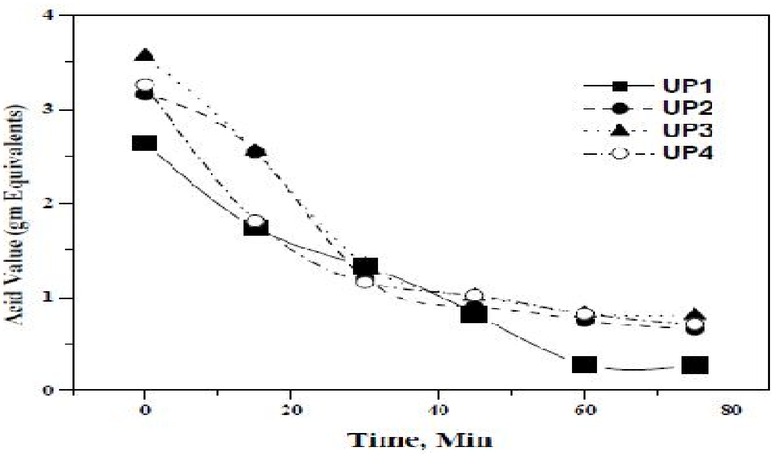

Fig 1: Acid value of all unsaturated acid UP1, UP2, UP3 and UP4 at different time intervals.

The extent of polymerization reaction is calculated from the acid value of Table 2 and its variation with time is plotted in Figure 2a. For all samples, the extent of reaction increases with time. The extent of reaction is very low at the initial period (<0.45 for the reaction time of fifteen minutes). The extent of reaction is not even 90 % after reacting for seventy-five minutes. It is observed from the figure that although at the initial period the extent of reaction follows no order among the various reaction mixtures but at higher time periods, the extent of reaction follows a definite trend. At higher time period, the extent of reaction is higher for UP1, whereas it is lower for UP4. The glycolyzed PET, GPET1, which is employed for the preparation of UP1, consists of small glycols, mainly BHET leading to its higher reactivity towards maleic acid, a diacid, thus showing higher extent of reaction.

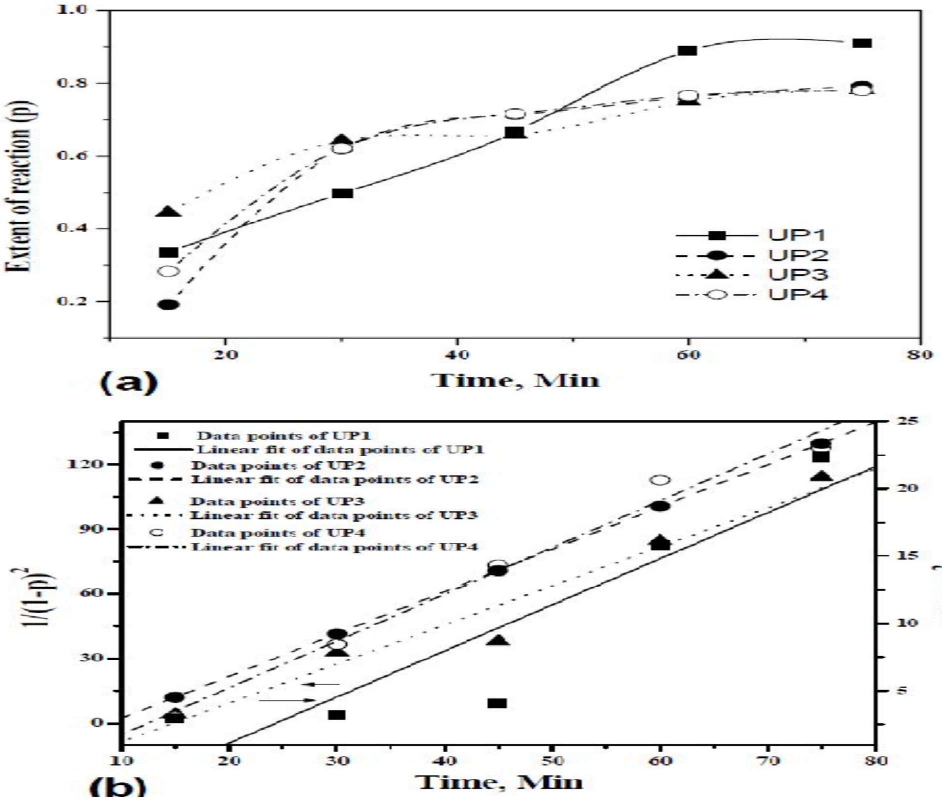

Fig 2: Plots of (a) extent of reaction of different unsaturated polyesters with time and (b) Average degree of polymerization of different unsaturated polyester with time.

As C0 is constant, the plot of $1/(1-p)^2$ versus time (t) will generate a straight line. The plots of $1/(1-p)^2$ with time are shown in Figure 2b. For the sake of clarity, the data points of UP1 are taken on different scales (the axis in the right hand side of the figure). The data points for all samples are linearly fitted. It is observed that the data fitted very well for all samples except for UP1, which shows large a deviation. The data points for UP1 indicate a sudden rise in reaction rate after forty-five minutes. From the slope of these linear plots, the value of rate constant (k) can be calculated and is observed to be almost the same for all samples. The value of r is 1.1 at the start of the process. The degree of polymerization is calculated from the extent of reaction (p) and constant r value. Although the ratio of carboxyl to hydroxyl group (r) should vary with the passage of time during the reaction, it is assumed as constant for calculation of degree of polymerization; otherwise, r is changing with the reaction. To get the exact value of r during reaction, one has to solve a tedious mathematical equation, which will be included in a later manuscript. The variations in the degree of polymerization (DPn) with time for all samples are shown in Figure 3. The degree of polymerization increases with elapsed time for all samples. This is in line with expectations, as the reacting chains are propagated to a large molecule with the passage of time. The degree of polymerization is almost similar for UP2, UP3 and UP4, whereas it is lower for UP1 compared to all three samples up to 45 minutes, beyond which a sudden rise in degree of polymerization for UP1 is observed. The diols, GPET1 used for the preparation of UP1 have a higher hydroxyl value compared to the other glycolyzed PET. The presence of maximum proportion of small diols (BHET) in GPET1 leads to its increased reactivity at sufficient time. Thus, the degree of polymerization increases very fast with time after forty-five minutes of polyesterification.

The measured acid value and the extent of reaction after seventy-five minutes of polyesterification for all samples are plotted as a bar diagram in Figure 4. The acid value and the extent of reaction are the lowest and the highest, respectively for UP1 whereas these are almost similar for the other three samples. As UP1 is prepared from the esterification reaction of short chain diols (BHET), GPET1 with maleic acid, the rate of reaction is much higher leading to the lowering of acid value and hence increase in the extent of reaction. The increase in the chain length of the reacting diols (oligomers of BHET) in the other three samples (UP2, UP3 and UP4) will lower the rate of polyesterification reaction, causing increment in the acid value and subsequent decrease in the extent of the reaction.

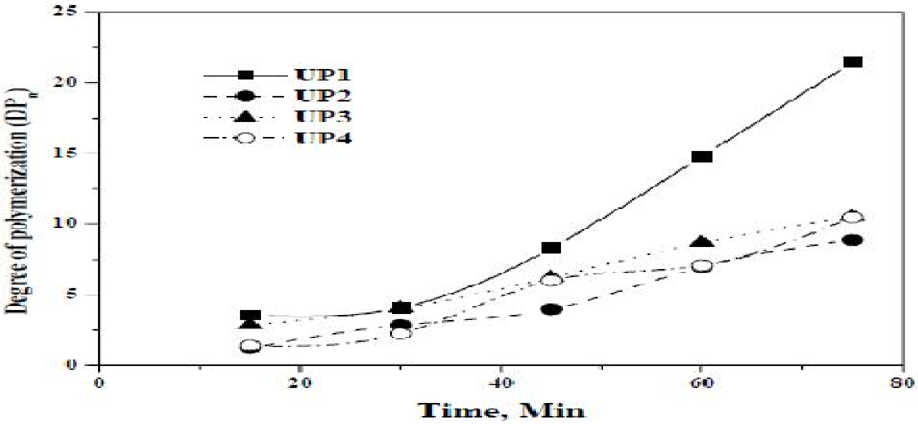

Figure 3: Degree of polymerization of different unsaturated polyesters with time.

CONCLUSION

A higher proportion of virgin PET in the mixture of waste and virgin PET consumes more glycols for the glycolysis process and gives rise to a glycolyzed PET (GPET1) which contains less amount of free glycol and shows the highest hydroxyl value. During the preparation of unsaturated polyester from glycolyzed PET, higher degree of polymerization (DPn), higher extent of reaction and lower acid value is observed for the polyesterification of GPET1. This is due to the presence of higher extent of BHET (Bis hydroxy ethylene teretpthalate) in the GPET1.

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