

Kinetic Study of Polyester Derived from Glycolyzed PET Waste With Varied Composition

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Abstract

In this investigation, the production of secondary value-added products, such as saturated polyester, derived from the glycolysis of poly(ethyleneterephthalate) (PET) is examined as an effective way for PET recycling. The glycolyzed PET (GPET) obtained was reacted with mixture of phthalic anhydride and glycol with varied composition and their reaction kinetic were studied. During polyesterification it was observed that degree of polymerization (DP_n) and extent of reaction (p) is increased, while acid value and hydroxyl are decreased with an increase in the GPET content in the reaction mixture. The well-defined order maintained up to 50% GPET content, beyond it the DP_n , and p followed decreasing trend with time.

Keywords: extent of reaction, GPET, PET, saturated polyester

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INTRODUCTION

Usual reactants for the saturated polyesters are a glycol and an acid or anhydride. It is the family of polyester in which the polyester backbones are saturated. PET a class of saturated polyester does not create a direct hazard to the environment but, due to its substantial fraction by volume in the waste stream and its high resistance to the atmospheric and biological agents, it is seen as a noxious material.^[1] PET glycolysis has been studied for many years.

The most frequently used glycols are ethylene glycol (EG), diethylene glycol (DEG), propylene glycol, and dipropylene glycol (DPG). PET is widely used in the packaging of beverages and drugs. In this paper, during synthesis of saturated polyester with GPET, phthalic anhydride, and ethylene glycol the kinetic study was studied. This has been done for the estimation of the maximum incorporation of GPET in the reaction medium.

EXPERIMENTAL SECTION

Glycolysis of PET Waste

Glycolysis of PET scrap was carried out in a five necked glass reactor equipped with a mechanical agitator assembly, a reflux condenser, nitrogen inlet/outlet, and a thermo-couple linked to a temperature regulation device. Molar ratio of PET to EG was taken 1:2, respectively. $Zn(CH_3COO)_2$ was used as transesterification catalyst. The time taken for complete glycolysis process was 8–10 h with temperature of 180–210 °C.

Synthesis of Saturated Polyester from Glycolyzed PET

Initially, a reference resin (STD PET) was synthesized by direct esterification. The overall reaction time, including the esterification and the polycondensation processes, is long and usually varies from 7 to 10 h. The above experiment was repeated by replacing the ethylene glycol with GPET by 100:0, 80:20, 60:40, 50:50, and 40:60%, respectively. The quantity of TA remains the same for all above

combinations. The samples were taken out at different time intervals to study the polymerization kinetics. The nomenclature used in this work is based on the original composition of reactants (shown in Table 1).

Table 1. Detailed Feed Composition of the Saturated Polyester.

Sample ID	GPET (%)	EG (%)
STD PET	0	100
GPET20	20	80
GPET40	40	60
GPET50	50	50
GPET60	60	40

CHARACTERIZATION

Acid Value Hydroxyl Value and Measurement of Extent of Reaction

The acid and hydroxyl value was determined by following the standard method NF T 52-114 and 113. The measurement of p is followed by our previous manuscript.

RESULTS AND DISCUSSION

Characterization of Saturated Polyester Resin

The acid and the hydroxyl value (mg KOH/gm) obtained during the synthesis of the saturated polyester (GPET based) at different time intervals are shown in Figures 1–4.

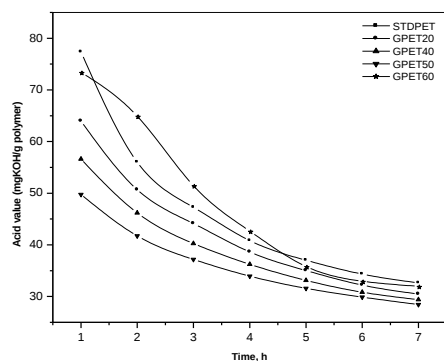


Fig. 1. Acid Values for the Different Saturated Polyester Resins at Different Time Intervals.

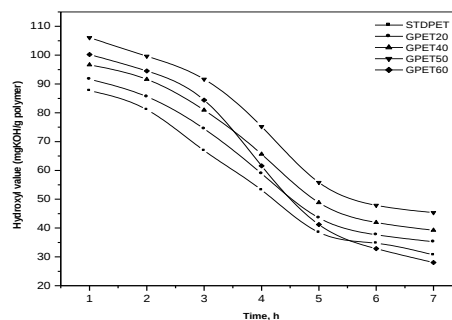


Fig. 2. Hydroxyl Values for the Different Saturated Polyester Resins at Different Time Intervals.

It is observed from the Figures 1 and 2 that for all the samples, with increase in the reaction time acid and hydroxyl values goes on decreasing.

The extent of polymerization reaction and $(DP)_n$ is calculated by equation

$$DP_n = \frac{1+r}{1+r-2pr}$$

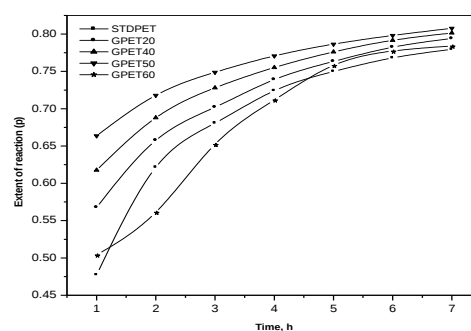


Fig. 3. Plots of Extent of Reaction for the Different Saturated Polyester Resins

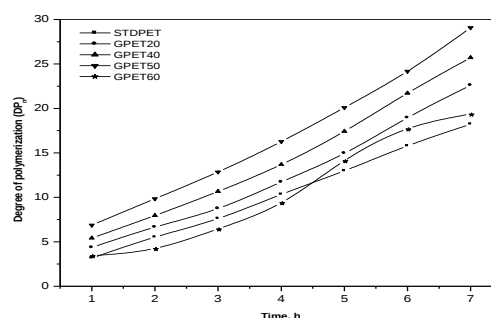


Fig. 4. Degree of Polymerization for the Different Saturated Polyester Resins at Different Time intervals

The extent of reaction is smaller for STDPET, while it is larger for the sample GPET50 during whole reaction time. The degree of polymerization increases with elapsed time for all samples.

CONCLUSION

In this investigation, GPET products (oligomers) obtained by glycolysis of PET were reacted with mixture of phthalic anhydride and glycol with different composition and their reaction kinetic were studied. This was done to estimate the maximum incorporation of GPET in the reaction medium. During polyesterification of GPET with varied composition, the degree of polymerization (DP_n) and extent of reaction (p) is observed to be increasing, while acid value followed decreasing trend with an increase in the GPET content in the mixture. The well-defined order maintained upto 50% GPET content beyond it, the (DP_n), and extent of reaction follows decreasing trend with time.

1. Sharma V., Kundu P.P., *J Polym Eng.* 2010; 29: 199–210p.