

Synthesis of Unsaturated Polyester Resin from Postconsumer PET Bottles: Effect of Type of Glycol on Characteristics of Unsaturated Polyester Resin

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ABSTRACT: Postconsumer PET bottles including water and soft-drink bottles were depolymerized by glycolysis in excess glycols, such as ethylene glycol, propylene glycol, and diethylene glycol, in the presence of a zinc acetate catalyst. The obtained glycolyzed products were reacted with maleic anhydride and mixed with a styrene monomer to prepare unsaturated polyester (UPE) resins. These resins were cured using methyl ethyl ketone peroxide (MEKPO) as an initiator and cobalt octoate as an accelerator. The physical and mechanical properties of the cured samples were investigated. It was found that the type of glycol used in glycolysis had a significant effect on the characteristics of the uncured and cured UPE resins. Uncured EG-based UPE resin was a soft solid at room temperature, whereas uncured

PG- and DEG-based resins were viscous liquids. In the case of the cured resins, the EG-based product exhibited characteristics of a hard and brittle plastic, while the PG-based product did not. The DEG-based product exhibited characteristics of hard and brittle plastic after strain-induced crystallization had occurred. In addition, it was also found that no separation of the type of bottles was needed before glycolysis, since UPE resins prepared from water bottles, soft-drink bottles, and a mixture of both bottles showed the same characteristics. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 788–792, 2003

Key words: polyesters; resins; polyethylene (PE)

INTRODUCTION

Poly(ethylene terephthalate) (PET) is widely used in packaging applications, especially in water and soft-drink bottles industries due to its clarity, light weight, and selective gas permeability.¹ However, postconsumer PET bottles are not reused by those manufacturers. They are left as “plastic waste,” causing an environmental problem since they cannot be degraded by natural processes. The effective solution to solve this problem is to recycle these postconsumer plastics. One recycle method that has been developed is to convert high molecular weight polymers into low molecular weight substances via chemical reactions. In regard to PET, it can be depolymerized by glycolysis in excess glycols. The components of the glycolyzed products, depending on the type of glycol used, are predominantly the monomers and the dimers of bis(hydroxyalkyl)terephthalate and terephthalates having fragments of different glycols in the same molecule.^{2–7} The glycolyzed products can be used as reactants for the preparation of other polymers such as unsaturated polyester (UPE) resins.^{3–6} However, each

work was mostly done by using only one type of glycol for glycolysis, such as ethylene glycol and propylene glycol. Therefore, this research emphasized the investigation of the characteristics of UPE resins when different glycols are used in the glycolysis of PET. Such characteristics include appearance, stress–strain behavior, hardness, and softening point.

EXPERIMENTAL

Materials

In the glycolysis of PET, three types of postconsumer PET bottles were used: water bottles, soft-drink bottles, and a mixture of soft-drink bottles and water bottles (1:1 by weight). Three types of glycols were used: ethylene glycol (EG), propylene glycol (PG), and diethylene glycol (DEG). In all reactions, zinc acetate was used as a catalyst. All glycols and zinc acetate were obtained from the Aldrich Co.

In the synthesis of UPE resin, the glycolyzed products, maleic anhydride (MA), hydroquinone, and the styrene monomer were used. The last three chemicals were obtained from the Aldrich Co.

For preparation of the cured resins, methyl ethyl ketone peroxide (MEKPO) was used as an initiator and cobalt octoate was used as an accelerator. These materials were obtained from the Siam Chemical In-

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TABLE I
Characteristics of Glycolyzed Products

Formula no.	Weight obtained (g)	Product appearance	Hydroxyl value (mg of KOH/g) before extraction	Hydroxyl value (mg of KOH/g) after extraction
W-EG	119.10	White powder	665	341
S-EG	115.50	White powder	550	362
M-EG	109.21	White powder	511	345
W-PG	248.60	Green transparent liquid	765	—
S-PG	230.50	Green transparent liquid	811	—
M-PG	241.64	Green transparent liquid	810	—
W-DEG	242.20	Green transparent liquid	850	—
S-DEG	241.50	Green transparent liquid	791	—
M-DEG	246.23	Green transparent liquid	865	—

W, water bottle; S, soft-drink bottle, M, mixture of water bottle and soft-drink bottle.

dustries Co. All materials were used as received without further purification.

Methods

Glycolysis of PET

Ground postconsumer PET bottles, a glycol (ratio of PET:glycol = 40:60 w/w), and zinc acetate, 0.5% of PET weight, were mixed in a 500-mL four-necked round-bottom flask connected with a stirrer, a thermometer, a condenser, and a N₂ gas inlet. The reaction was carried out at 190°C for 8 h under a nitrogen atmosphere. Then, the mixture was allowed to cool to room temperature under a nitrogen atmosphere. Distilled water was added and the precipitate was collected. The hydroxyl values (ASTM D2849 Method A)² were determined before and after water extraction.

Synthesis and analysis of UPE resin

The glycolyzed product and maleic anhydride (ratio of hydroxyl:carboxyl = 1.1:1)³⁻⁵ were mixed in a 500-mL four-necked round-bottom flask connected to a stirrer, a thermometer, a condenser, and a N₂ gas inlet. The reaction was carried out at 200°C for 10 h under a nitrogen atmosphere. Then, hydroquinone, 0.45% of PET weight, was added into the hot resin for preventing the resin from curing before use. The resin was allowed to cool to room temperature under a nitrogen atmosphere; then, it was dissolved in a styrene monomer (30% w/w of the resin).

The synthesized UPE resin and cobalt octoate were mixed together until the mixture was homogeneous; then, MEKPO was added to the mixture. The ratio of UPE:cobalt octoate:MEKPO was 100:0.5:0.5. The mixture was poured into a mold and then left at room temperature until it hardened. Then, the hardness (ASTM D2240⁸ with Durometer Shore D), stress-strain behavior (ASTM D 790M⁹ with LLOYD 500), and Vicat

softening point (ASTM D 1525¹⁰ with Vicat tester) of the samples were determined.

RESULTS AND DISCUSSION

After cooling to room temperature, the EG-based glycolyzed products precipitated from the reaction mixture, whereas the PG-based and DEG-based glycolyzed products did not precipitate. Furthermore, after water extraction, it was very easy to collect the precipitates of the EG-based glycolyzed products, while no or little precipitation was observed for the PG-based and DEG-based glycolyzed products. Consequently, the white powders obtained after water extraction when EG was used in the glycolysis were used as the glycolyzed products. On the other hand, the transparent liquids obtained from glycolysis using PG and DEG were used as the glycolyzed products without water extraction. The green color of the liquid was from the pigments in the PET bottles. (See Table I).

The above observation combined with the results of the hydroxyl values before water extraction suggest that PG-based and DEG-based glycolyzed products contain more lower molecular weight molecules than

TABLE II
Hardness and Vicat Softening Points of Cured UPE Resins

Formula no.	Hardness Shore D	Vicat softening point (°C) ^a
W-EG	68 ± 7	>150 ± 10
S-EG	59 ± 6	>150 ± 10
M-EG	58 ± 11	135 ± 10
W-PG	59 ± 5	>150 ± 10
S-PG	78 ± 3	130 ± 10
M-PG	81 ± 7	138 ± 10
W-DEG	78 ± 10	>150 ± 10
S-DEG	73 ± 9	>150 ± 10
M-DEG	69 ± 8	>150 ± 10

^a Vicat tester cannot detect temperature above 150°C.

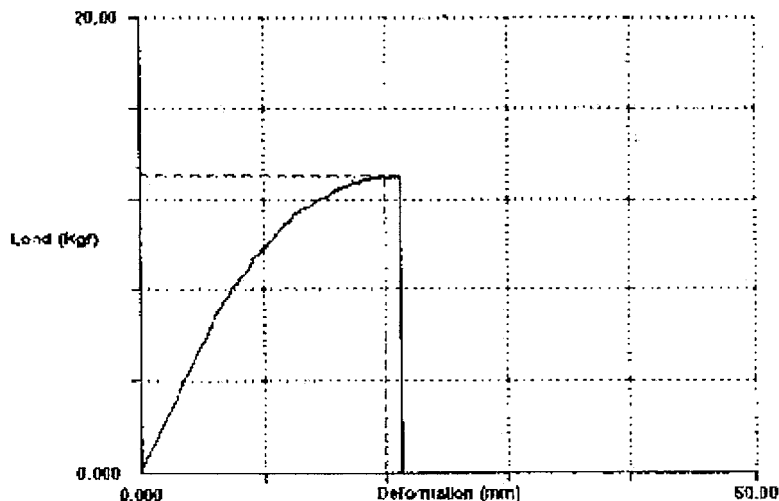


Figure 1 Stress-strain curve of cured UPE resin prepared from postconsumer PET water bottle and EG.

do the EG-based glycolized products. The hydroxyl values before water extraction of all products indicate that there are unreacted glycols in the products. The hydroxyl values after water extraction of EG-based glycolized products also indicate that the products consist mostly of the monomer and dimer of bis(hydroxyethyl) terephthalate (BHET) since their hydroxyl values are in between those of pure BHET (441.5) and its dimer (251.3).²⁷ These results suggest that the type of glycols affects the characteristics of the obtained glycolized products, whereas the type of bottles does not.

It was found that hot UPE resins obtained from EG-based glycolized products had a very high viscosity. At room temperature, the resins were a soft white solid and could not dissolve in the styrene monomer. Therefore, heating to about 100°C was needed to dissolve them in the styrene monomer. However, when the resins were cold, they became solid again. This

caused a problem in the casting process because heating of the resins was needed before pouring them into the molds. In the case of UPE resins prepared from PG-based and DEG-based glycolized products, they were highly viscous liquids at room temperature. This is the result of the presence of unreacted glycols in the glycolized products. These glycols can react with maleic anhydride and form lower molecular weight molecules. Consequently, UPE resins were in liquid form and easy to dissolve in the styrene monomer without heating. Besides, after mixing with the styrene monomer, PG- and DEG-based UPE resins were still in a liquid form but at a lower viscosity at room temperature. This characteristic resembles as that of commercial UPE resin (obtained from the Siam Chemical Industries Co.).

It was also found that when the same glycol was used there was no difference in the product character-

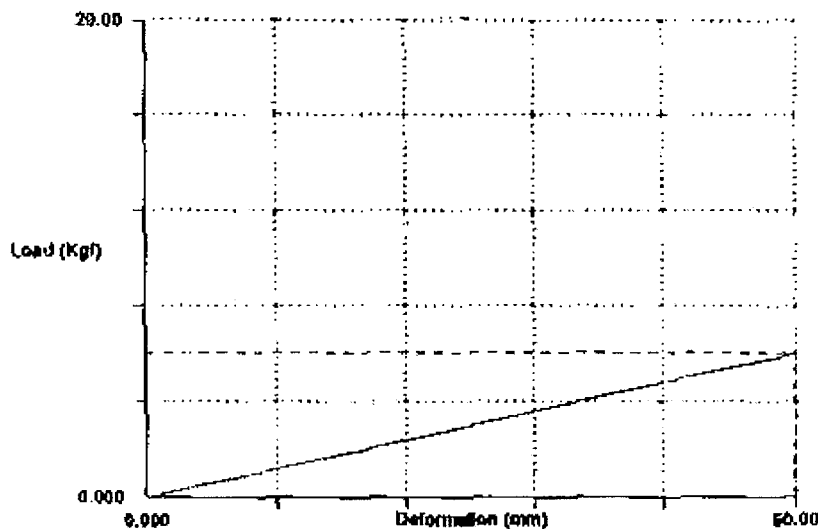


Figure 2 Stress-strain curve of cured UPE resin prepared from postconsumer PET water bottle and PG.

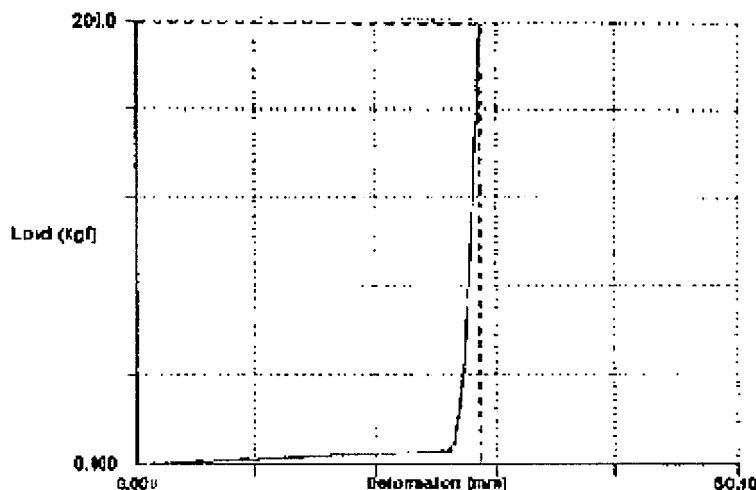


Figure 3 Stress-strain curve of cured UPE resin prepared from postconsumer PET bottle water and DG.

istics between all UPE resins obtained from water bottles, soft-drink bottles, and the mixture of both bottles. This result indicates that additives added to these bottles do not affect the characteristics of all UPE resins. This suggests that no separation of the type of bottle is needed for the UPE resin synthesis.

The cured products obtained from EG-based UPE resins were a light yellow, opaque solid, while those obtained from DEG-based UPE resins were a yellow, slightly translucent solid. Those obtained from PG-based UPE resins were a yellow, translucent solid. The difference in translucency of these products may result from the difference in the degree of crystallinity, which is due to the regularity of the UPE molecules. It can be seen that these products are different in molecular composition. EG-based resins contain only EG segments. This suggests that they have a most regular structure. On the other hand, PG-based resins contain both EG (from PET bottles) and PG segments. This suggests that they have the least regular structure. As a result, it is easier for the former to form more crystalline regions, causing the sample to be opaque.

From Table II, the type of glycol does not clearly show the effects on the hardness and Vicat softening points of the cured UPE resins. The variations of these properties are high. This is because the methods used for the determination of these two properties concern the study of very small specific areas of the samples. It is possible that the indentors of the durometer and the Vicat tester were pressed on an amorphous area at one time, while on crystalline area at another time. Consequently, their values are different.

However, the type of glycol has a great effect on the stress-strain behavior of the cured UPE resins as shown in Figures 1–3, which are the examples of the stress-strain curves observed in the bending test. The EG-based product has a hard and brittle behavior and

the sample breaks after receiving a significant load, as shown in Figure 1. On the other hand, the PG-based product elongates as the load was increased and does not break, as shown in Figure 2. The curve stops as the sample reaches the machine limit. For the DEG-based product, the sample elongates as the load increases but the curve suddenly rises, indicating that a high load is needed to extend the sample. The curve stops as the load reaches the machine limit.

This can be explained by considering the structures of the resins. As previously mentioned, the EG-based resin has the most regular structure since it has only EG segments in the molecules. Therefore, besides the crosslinking that occurs due to the curing process, the molecules also orient and pack to form crystalline regions. This increases the stiffness of the molecules, so at a significant load, the sample breaks. For PG-based resin, the molecules are composed of EG (from PET bottles) and PG segments; consequently, it is very difficult for the resin to form crystalline regions, and mostly amorphous regions are formed. Therefore, the molecules are easy to extend as the load is applied. For the DEG-based resin, the curve shows the occurrence of strain-induced crystallization. At first, the molecules of the DEG-based resin composed of EG and DEG segments do not perfectly pack and form crystalline regions. However, as the load is applied, the molecules extend, and since the structures of EG and DEG are almost similar, they form crystalline regions as the molecules perfectly align. The resin then becomes suddenly stiff and a higher load is needed to bend the sample.

It was observed that cured UPE resins prepared from different types of bottles using the same glycol had the same appearance, exhibited the same stress-strain behavior, and had comparable hardness and Vicat softening points as shown in Table II. These

results indicate that type of bottles did not affect the characteristics of the UPE resins.

CONCLUSIONS

Postconsumer PET bottles were depolymerized by glycolysis with glycols, such as EG, PE, and DE in an excess condition. The obtained glycolyzed products were used to synthesize UPE resins. The results showed that the type of glycol had a significant effect on the characteristics of the glycolyzed products and the uncured and cured resins. The preparation and handling of the PG- and DEG-based UPE resins were easier than those of the EG-based UPE resins since the former two were in liquid form. The results also showed that the type of bottle did not affect the characteristics of the synthesized UPE resins. This suggests that no separation of bottles is needed.

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