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Mechanical Property Improvement of UPE Resin from Glycolyzed PET with Commercial UPE Resin

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Abstract

The aim of this research paper is to improve mechanical properties of cured unsaturated polyester (UPE) resin prepared from glycolyzed PET by mixing with a commercial UPE resin. Postconsumer PET bottles were depolymerized by glycolysis reaction in excess propylene glycol at 190ºC in the presence of zinc acetate as a catalyst. The glycolyzed product was polyesterified with maleic anhydride and mixed with styrene monomer in order to obtain UPE resin. The prepared UPE resin was mixed with a commercially available general purpose grade UPE resin at various ratios. The mixed resins were cured using methyl ethyl ketone peroxide and cobalt octoate. Comparing between the prepared and commercial resins, it is most likely that the cured product from prepared resin possessed a higher crosslink density than the cured commercial resin. The results showed that the hardness of cured resin prepared from glycolyzed PET was slightly higher than that of the cured commercial resin. The addition of commercial resin did not affect the hardness of mixed resins. The impact strength and flexural strength increased as the amount of commercial resin increased. However, at higher than 60% by weight of the commercial resin, the improvement was leveled off.

Key words : PET, Recycling, Glycolysis, Unsaturated polyester

Introduction

Poly(ethylene terephthalate) (PET) is a semicrystalline thermoplastic polyester commonly used as a raw material for the production of textile fibers and films as well as for the packaging application. Most soft-drink bottles are made of PET due to its superior mechanical properties, clarity and selective gas permeability. Inevitably, the volume of post-consumer PET waste has rapidly increased. As PET waste is practically difficult to eliminate, recycling of PET waste is of interest to many researchers(Awaja and Pavel, 2005) in particular by the chemical approach.(2) The principle of chemical recycling is to convert high molecular weight polymers into low molecular weight substances via chemical reactions. PET can be depolymerized into smaller molecules via glycolysis reaction in excess glycols. The components of the glycolyzed products, depending on the type of glycol used, are predominantly monomers and oligomers of bis(hydroxylethyl)terephthalate (BHET) having fragments of different glycols in the same molecule.(3) The obtained glycolyzate or glycolyzed product can then be used as a starting ingredient for synthesis of other polymers with higher economical values, such as unsaturated polyester resins(Vaidya and Nadkarni, 1987 and 1988) urethane oils(Saravari, *et al*. 2004), etc. Apart from PET waste from post-consumer soft-drink bottles, it was reported that PET from fibers (Ghaemy and Mossaddegh, 2005) and fabrics (Potiyaraj, *et al*, 2007) can also be glycolyzed and subsequently used for synthesis of commercial value added products.

UPE resins are widely used as a matrix for fiber-reinforced composites which are a current alternative to conventional structural materials like steel and wood in a broad range of engineering applications. The widespread use of UPE resins in the fiber-reinforced composites industry is due to their low cost and the wide variety of grades available to meet specific requirements. The synthesis of unsaturated polyester (UPE) resins from the glycolyzed product of PET has been studied extensively.(9)

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In general, mechanical properties of cured resins prepared from glycolyzed PET were lower than those of cured resins from commercially available resins to some extent. Types and compositions of glycols used during glycolysis reaction significantly affected physical properties of cured UPE resins.(10) It was found that the glycolyzed product obtained using diethylene glycol (DEG) gave overall better mechanical properties.(11) Mechanical properties of cured resin prepared from DEG were slightly lower than those of virgin commercial products.(12) However, the higher cost of DEG compared with propylene glycol (PG) or ethylene glycol (EG) may hinder its practical use.

In this present study, physical properties of cured UPE resins obtained from the mixtures of UPE resin prepared from glycolyzed PET and a commercially available UPE resin at various ratios were investigated. It was proposed that the mechanical properties of the mixed UPE resin would be improved compared with those of UPE resin merely prepared from glycolyzed PET.

Materials and Experimental Procedures

Materials

Post-consumer soft-drink PET bottles of the same brand were collected and cleaned. The bottles were cut into small pieces and oven-dried. The dried PET waste was pulverized and sieved in order to obtain PET waste powder with a particle size of less than 0.5 mm. Propylene glycol (PG) and zinc acetate were used in glycolysis reaction. Maleic anhydride (MA), hydroquinone, and styrene monomer were used for UPE synthesis. All chemicals used in the glycolysis and polyesterification reactions, unless otherwise stated, were of reagent grade and supplied by Fluka. They were used as received without further purification.

In order to prepare cured polyester products, methyl ethyl ketone peroxide (MEKPO) was used as an initiator and cobalt octoate was used as an accelerator. These chemicals, as well as a commercially available general purpose grade UPE resin, were kindly provided by Siam Chemical Industry (Samutprakarn, Thailand). This commercial resin, as reported by the producer, was prepared from neopentyl glycol, isophthalic acid and maleic anhydride. All materials were also used as received without further purification.

Glycolysis of PET

Pulverized PET waste was reacted with PG with the molar ratio of PET repeating unit to PG of 0.5:1.0.(13) Zinc acetate was used as a catalyst at 0.5% by weight of PET. The glycolysis was carried out in a four-necked round-bottom flask attached with a mechanical stirrer, a thermometer, a reflux condenser, and a nitrogen gas inlet. The reaction proceeded for 8 hr under nitrogen atmosphere while the temperature was maintained at 190°C. The glycolyzed product was then allowed to cool down to room temperature under nitrogen atmosphere. Gel permeation chromatography (Waters GPC system, Milford, MA, USA) and a Brookfield RVT viscometer (Middleboro, MA, USA) were used to analyze the average molecular weight of the glycolyzed product and its viscosity, respectively. It was subsequently analyzed by a Perkin Elmer System 2000 Fourier transform infrared spectrometer (FT-IR, Wellesley, MA, USA).

Synthesis of UPE Resins

The glycolyzed products and maleic anhydride were mixed in a 1000 mL four-necked round-bottom flask fitted with a stirrer, a thermometer, a distillation condenser, and a nitrogen gas inlet. Mixing took place at a fix molar ratio of 1.1:1(13) for the hydroxyl-to-carboxyl groups. The reaction was brought up to 180°C in 1 hr under nitrogen atmosphere. The temperature was then raised to 200°C and was retained for 6 hr under nitrogen atmosphere. Water occurring from the reaction was removed all through. Hydroquinone, about 0.045% w/w of the resin, was added immediately at the end of the reaction in order to prevent the resin from prematurely curing. After cooling down to 100°C under a nitrogen atmosphere, the resin was dissolved in a styrene monomer to obtain 35% w/w styrene in the resin.(4)

The prepared UPE resin was mixed with a commercial UPE at various ratios. The amount of the commercial UPE was varied from 0 to 100% by weight. The mixtures of UPE resins were analyzed by a Brookfield RVT viscometer (Middleboro, MA, USA) and a Perkin Elmer System 2000 FT-IR spectrometer (Wellesley, MA, USA).

Curing of UPE Resins

The mixed UPE resin and cobalt octoate as an accelerator were mixed together until the mixture was homogeneous. MEKPO as an initiator was added to the mixture in order that the ratio of UPE:cobalt octoate:MEKPO was 100:0.5:0.5. The mixture was poured into a silicone mold and located in an oven for curing at 100°C for 24 hr. Gel time and cure time of the resins were determined from the exotherm temperature profile obtained during the course of curing.

Testing of Physical Properties

According to ASTM D3418-03, differential scanning calorimetry analysis (DSC) was performed using Netzsch DSC200 (Burlington, MA, USA) by heating from -50 to 200°C at a heating rate of 10°C/min under nitrogen atmosphere. Midpoint temperature was designated as glass transition temperature (T_g). Thermal stability analysis was carried out with a Mettler Toledo thermal gravimetric analyzer (TGA) (TGA/SDTA 851, Columbus, OH, USA) based on ASTM D3850-94. The scans were obtained by heating from 0 to 1000°C (static heating at 1000°C, 5 min) at a heating rate of 10°C/min under nitrogen atmosphere. Onset thermal degradation temperature was determined from the obtained weight loss curve at 5% weight loss.

Hardness of the cured products was investigated based on ASTM D2240-86 with a Shore D durometer (Freeport, NY, USA). The samples were tested for charpy impact strength using an impact strength tester complying with ASTM D6110-02 (ATS FAAR, Milan, Italy). A universal testing machine (Lloyd L500, Fareham, UK) was used for determining the flexural strength by the three-point bending method following ASTM D790-02. The fracture morphology of the samples was observed by a scanning electron microscope (JEOL JSM-6400 SEM, Tokyo, Japan).

Results and Discussion

Post-consumer PET bottles were depolymerized with PG in the presence of zinc acetate as a catalyst. The obtained glycolyzed product was a clear greenish liquid with a viscosity of 800 centipoises. The color of the glycolyzed product was due to the additives used in PET manufacturing. Figure 1 shows the FT-IR spectrum of the glycolyzed product. The absorptions at 3200-3600, 2800-3000, 1600-1800, and 1100 cm^{-1} are due to –OH, -CH, C=O, C-O-C and C-OH stretchings, respectively. These absorption peaks implied the presence on compound and/or compounds having hydroxyl and ester groups.(6) The peak of hydroxyl groups was broad with low %transmittance because PET molecules were depolymerized into shorter molecular chains and the end groups of each chain were hydroxyl groups. The number average molecular weight of the glycolyzed product was 704, which is comparable to the molecular weight of oligomers that have 1-3 monomeric units of bis(hydroxypropyl)terephthalate.(14) This implies that the extent of polymerization is considerable and the glycolyzed product mainly consists of hydroxyl-terminated monomer, dimer and trimer.(4)

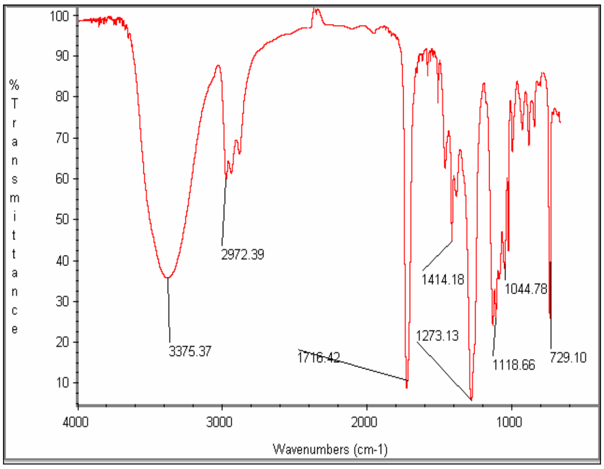


Figure 1. FT-IR spectrum of glycolyzed waste PET bottles.

The product obtained from polycondensation of the glycolyzed product and MA was a highly viscous liquid. Styrene monomer was added in order to obtain the UPE resin. The viscosity of the prepared resin was 1310 centipoises while that of the commercial resin was 345 centipoises. This was due to the fact that the commercial UPE resin contained 50% by weight of styrene monomer whereas the prepared UPE resin had only 35% by weight of monomer. The higher viscosity also came from a broad molecular weight distribution of the prepared resin.(4)

As shown in Figure 2, the FT-IR spectrum of the prepared resin exhibits absorption peaks at 3400-3600, 2900-3000, 1700-1800, 1600-1700, 1200-1300, 1100, 877 and 776 cm^{-1} which correspond to –OH, propylene glycol, C=O, C=C, C-O, reacted terephthalic acid, para disubstituted aromatic ring, and aromatic ring of styrene, respectively. The absorptions at 2900-3000 and 3400-3600 cm^{-1} were broad as a result of excess propylene glycol left unreacted from the glycolysis reaction, and hydroxyl groups left unreacted from polyesterification reaction. It has been reported that there were some glycols left after depolymerization(6) and polyesterification.(12) The FT-IR spectrum of the commercial UPE resin as shown in Figure 3 was similar to that of the prepared resin except for the absence of an absorption peak at 877 cm^{-1} of para disubstituted aromatic ring of terephthalic acid, while the peak at 736 cm^{-1} of meta disubstituted aromatic ring of isophathalic acid was present instead.

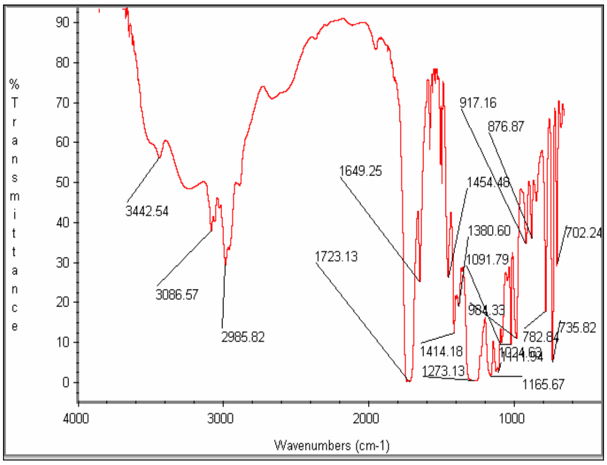


Figure 2. FT-IR spectrum of the prepared UPE resin from glycolyzed PET.

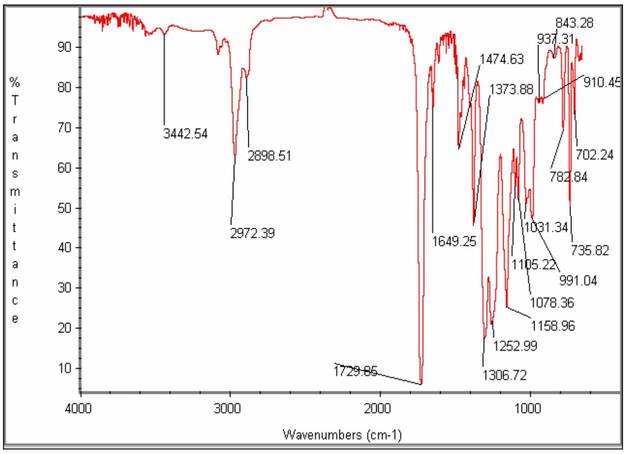


Figure 3. FT-IR spectrum of the commercial UPE resin.

As reported in Table 1, the gel time of UPE resin prepared from glycolyzed PET was considerably longer than that of the commercial UPE resin. The amount of hydroquinone in the prepared resin was much higher than that in the commercial UPE, thus prevent the commencement of crosslinking reaction. However, the duration between gel time and cure time of both resins was comparable indicating that the crosslinking rate in the prepared resin was as good as that in the commercial resin.

The glass transition temperature (T_g) as analyzed by DSC is shown in Figure 4. The exotherm of reaction related to the crosslinking process and to the thermal polymerization of UPE resins. T_g of the prepared resin varied from 67 to 70°C which was much lower than that at 130°C of the commercial resin. The onset degradation temperature (T_d) of the prepared and commercial resins was analyzed by TGA as shown in Figure 5. T_d of the resin obtained from glycolyzed PET was also lower than that of the commercial resin. The inferior thermal properties were due to the fact that the prepared resin contained molecules of various molecular sizes, from very short ones to longer ones, while the molecular chains of commercial resin were longer and distributed in a more consistent manner. It was pointed out that short molecular chains can act as plasticizer (12), thus lowering the T_g of the prepared resin.

Table 1. Curing characteristics of prepared and commercial resins.

	Gelation point		Curing point		
	Gel time (min)	Temp. at gel time (ºC)	Cure time (min)	Temp. at cure time (ºC)	Crosslinking duration (min)
Prepared resin	190	35	205	113	15
Commercial resin	16	33	33	174	17

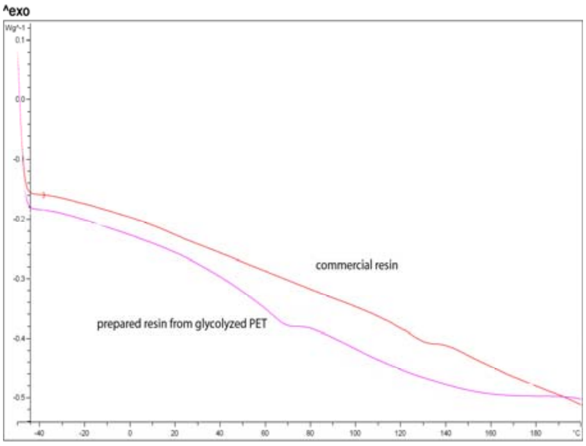


Figure 4. DSC thermogram of prepared and commercial resins

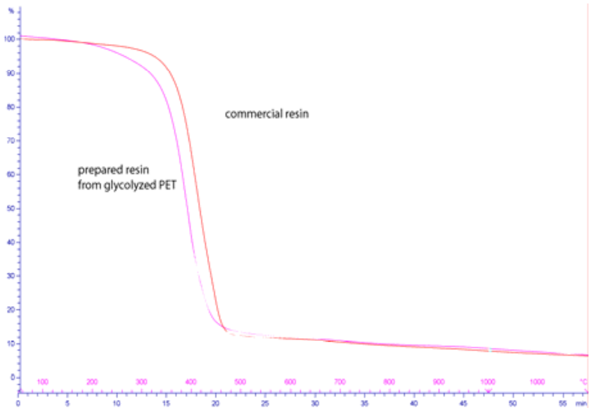


Figure 5. TGA thermogram of prepared and commercial resins.

The glycolyzed PET based UPE resin was mixed with 0 to 100% by weight of the commercial UPE resin. It was found that the viscosity of the mixture decreased as the amount of the commercial UPE resin increased. The gel time and cure time also decreased with the increasing amount of the commercial UPE resin.

The hardness of cured resins is shown in Figure 6. The hardness of cured product prepared from glycolyzed PET was slightly higher than that of cured commercial resin. In the prepared resin, the presence of terephthalate repeating units between crosslink points generated the harder domains and better separation between crosslink points in the packed crosslinked structure, thus resulting in a higher hardness.(4) With the addition of commercial resin, the hardness of mixed resin was not changed significantly.

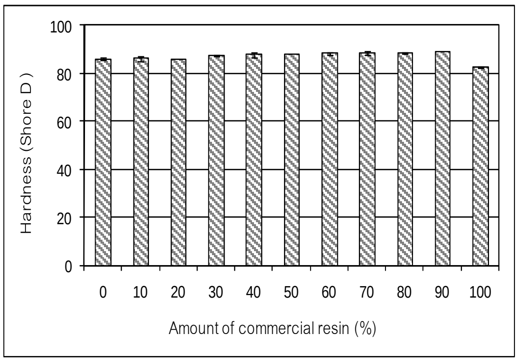


Figure 6. Hardness of cured resins.

Figure 7 shows the impact strength of cured resin. The cured commercial resin possesses slightly higher impact strength than the prepared resin. The higher toughness was owed to higher flexibility of the commercial resin molecular chains. The longer distance between the curable double bonds enabled the cured resin to have a lower crosslink density with more freely moving molecular chains.(8) The mixed resin with 60% by weight of commercial resin showed the highest impact strength in this field. The impurities and residues presented in the prepared resin may act as a stress distributor(15), thus improving the impact strength of the mixed resin.

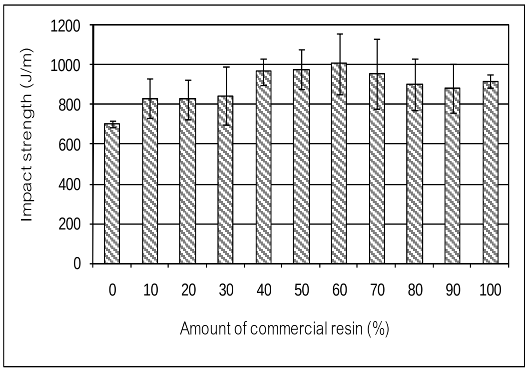


Figure 7. Impact strength of cured resins.

The results as shown in Figure 8 indicate that the flexural strength was improved as the amount of the commercial UPE increased. The longer distance between reactive double bonds existing in the commercial resin compared to that in the prepared resin enabled the cured commercial resin to have a lower crosslinking density and thus to become more flexible.(16) Conversely, the cured resin prepared from glycolyzed PET with a higher crosslinking density retained a higher compressive strength. The following statement can be formulated with respect to the classical beam theory: when material is subjected to bending test, a specimen must endure both compressive and tensile forces and the bending modulus has an intermediate value between the tensile and compressive moduli.(17) Due to its high crosslink density, the cured resin prepared from glycolyzed PET lacked of flexibility, thus lowering the flexural strength. The mixed resins, which encompassed the flexibility of commercial resin, therefore improved the flexural strength of the cured products, especially at 60% by weight of commercial resin. The slightly declining trend in impact and flexural strength of mixed resin at higher ratios may have also arisen from the difference between chemical structures of the prepared and commercial resins which were incompatible to some extent. (12)

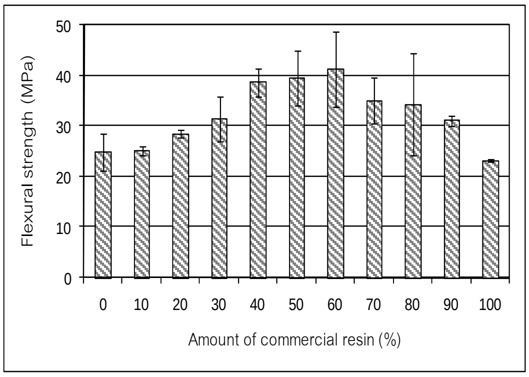
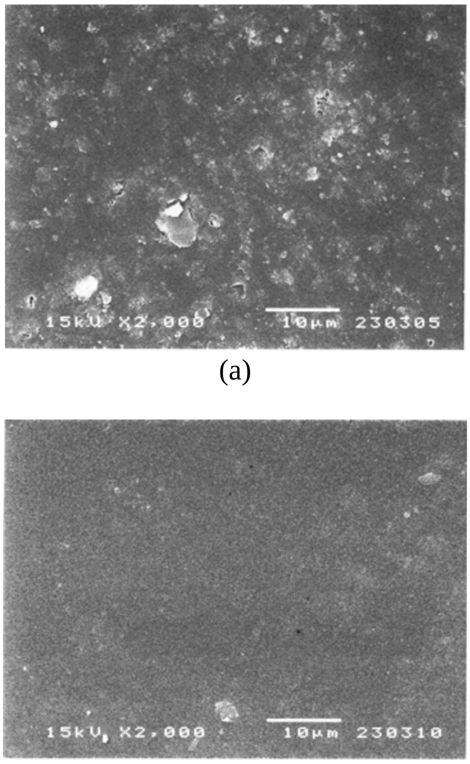


Figure 8. Flexural strength of cured resins.

The morphology of cured products as revealed by SEM at 2000× is shown in Figure 9. It was found that some additive residues were distributed and aggregated in the cured resin from glycolyzed PET. However, SEM micrograph of the cured commercial resin does not show residues or impurities in the polyester matrix. Although these small particles may attribute to the overall inferior mechanical properties of the prepared resin, they may, on the other hand also act as a stress distributor and contribute to better impact strength.(15)



(a)

(b)

Figure 9. SEM micrographs at 2000× of the fracture surface of (a) cured resin prepared from glycolyzed PET and (b) cured commercial resin.

Conclusion

A commercially available general purpose grade UPE resin was added into UPE resin prepared from glycolyzed PET at different ratios in order to improve mechanical properties of cured resins. Chemical structures of the prepared and commercial resins caused differences in their crosslinking characteristics as evidenced by the changes in glass transition and degradation temperatures. The hardness of the prepared resin was almost unchanged with the incorporation of the commercial resin. The results also indicate that the impact and flexural strength of the prepared resin were improved to a maximum of 44% and 40%, respectively, with the addition of the commercial resin. Practically, although the enhancement of mechanical properties is satisfactorily achieved with the addition of commercial resin, the increasing cost must also be taken into account.

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