

Physical Properties of Unsaturated Polyester Resin from Glycolyzed PET Fabrics

P. Potiyaraj, K. Klubdee, T. Limpiti

Department of Materials Science, Faculty of Science, Center of Excellence in Textiles, Chulalongkorn University, Bangkok 10330, Thailand

Received 23 December 2005; accepted 11 November 2006

DOI 10.1002/app.25923

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Physical properties of unsaturated polyester resins (UPE resins) prepared from glycolyzed poly (ethylene terephthalate) (PET) and PET/cotton blended fabrics were investigated. Initially, PET and PET/cotton blended fabrics were chemically recycled by glycolysis. The depolymerizations were carried out in propylene glycol with the presence of zinc acetate as a catalyst. The reaction time was varied at 4, 6, and 8 h. The glycolyzed products were then esterified using maleic anhydride to obtain UPE resins. The prepared resins were cured using styrene monomer, methyl ethyl ketone peroxide, and cobalt octoate as a crosslinking agent, an initiator and an accelerator, respectively. The cured resin products were tested for their me-

chanical properties and thermal stability. The results indicated that, among the fabric based resins, one prepared from the 8-h glycolyzed product possessed the highest mechanical properties those are tensile strength, tensile modulus, flexural strength, impact strength, and hardness. The highest thermal stability was also found in the cured resin prepared from the 8-h glycolyzed product. The mechanical properties of fabric based resins were slightly lower than those of the bottle based resin. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2536–2541, 2007

Key words: recycling; polyesters; esterification; mechanical properties; thermal properties

INTRODUCTION

Poly (ethylene terephthalate) (PET) is a thermoplastic polyester possessing excellent thermal and mechanical properties. Tremendous quantities of this material are consumed in the manufacture of video and audiotapes, X-ray films, food packaging especially soft-drink bottles, including the production of fibers for ropes, needlework (monofilament), fabrics as well as brushes for domestic cleaning.¹ It should be pointed out, that PET does not create a direct hazard to the environment but, because of 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.² This is the main driving forces responsible for the increased efforts focusing on PET recycling.³

Chemically, PET can be recycled by hydrolysis, acidolysis, alkalolysis, aminolysis, alcoholysis, and glycolysis.⁴ Glycolysis is the breakdown of the ester linkages by a glycol with the presence of a catalyst, resulting in oligomers or oligoester diols/polyols with hydroxyl terminal groups.⁵ Baliga and Wong

found that the amount of repeating units in the glycolyzed product depended on the catalyst used.⁶ They also pointed out that zinc acetate is the best in terms of the extent of depolymerization.

These glycolyzed products have been utilized as starting ingredients for the synthesis of polyurethanes, unsaturated polyesters (UPE resins), and saturated polyester plasticizers.^{7–11} Basically, the glycolyzed products can be brought into unsaturated polyester resin by esterification reaction. It was indicated that the type of glycol used in glycolysis had a significant effect on the characteristics of the cured UPE resins.¹² The propylene glycol based products exhibited less brittle characteristic than the ethylene glycol based products.¹⁰ In addition, it was 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.

While most of the recent research about PET recycling has been focused on recycling of soft-drink PET bottle, and more recently of PET fiber,¹³ with glycolysis reaction, this research studied the recycling of PET and PET/cotton blended fabrics. UPE resins were prepared from glycolyzed PET and PET/cotton blended fabrics under different reaction times. Mechanical properties and thermal stability of cured products were then investigated.

Correspondence to: P. Potiyaraj (pranut.p@chula.ac.th).

Contract grant sponsor: Graduate School, Chulalongkorn University.

EXPERIMENTAL

Preparation of unsaturated polyester resins

PET and PET/cotton woven fabrics were obtained from a local fabric producer. The PET/cotton fabric is at 65 : 35 blended ratio of PET : cotton by weight which is generally called T/C fabric. Our preliminary study pointed out that the glycolysis reaction would not be occurred with the presence of cotton in T/C fabrics. Thus, concentrated hydrochloric acid, a product of Merck, was used for elimination of cotton prior to glycolysis. Hydrolysis reaction was carried out at ambient temperature overnight. The hydrolyzed fabric was neutralized by rinsing several times with water. Use of acid for elimination of cotton may give some environmental concerns because of its ecological unfriendly. As a matter of fact, acid hydrolysis is used in the textile industry as a method for producing lightweight polyester fabrics from T/C fabrics. Research has been carried out to reduce the amount of acid in such process by using cellulase enzyme.¹⁴

PET and T/C fabrics were reacted with propylene glycol (PG) at the molar ratio of 1 : 2. Zinc acetate was used as a catalyst at the amount of 0.5% of fabric weight. Both propylene glycol and zinc acetate were reaction grade and produced by Fluka. Glycolysis reaction was carried on for 4, 6, and 8 h at 220°C under nitrogen atmosphere. At the end of the reaction, the reaction mixture was filtered. The filtrate was identified as glycolyzed products which were then checked for the viscosity using a Brookfield RVT viscometer. To obtain the yield of the glycolysis, a weighed quantity of the glycolyzed product was extracted with water and filtered. The filtrate containing water, PG, monomer, dimer, and probably some higher oligomers such as trimer, was concentrated by evaporation and then chilled in a refrigerator at 4°C overnight to precipitate out the oligomers. The dry-weight of the residue remaining after the first and second filtration was used to calculate the yield of glycolysis.⁶ The hydroxyl value (HV) of the extracted glycolyzed products was analyzed according to ASTM D4274-05 Method C.

Maleic anhydride (MA), a product of Fluka, was used to esterify the glycolyzed products. It was added to the glycolyzed products so that the molar ratio of OH/COOH was 1.1 : 1 HV of the glycolyzed products before extraction. The reaction was kept under nitrogen atmosphere at 180°C for at least 6 h in order that the acid value (AV) of the reaction mixture was about 60 mg KOH/g. The AV was determined by volumetric method to ensure that the equilibrium is reached.^{15,16} When the reaction finished, 0.45% by weight of hydroquinone, produced by Fluka, was added as an inhibitor to prevent gelation before casting. A Perkin-Elmer System 2000 Fourier

transform infrared spectrometer (FTIR) was employed to analyze the glycolyzed products as well as the esterified products.

Styrene monomer, supplied from Eternal Resin Co., was used as a crosslinking agent. After cooling the glycolyzed products down to 100°C, 35% by weight of styrene monomer was added as a crosslinking agent. Cobalt octoate, supplied from Thai Mitsui Co., (Thailand) and Methyl Ethyl Ketone Peroxide, a product of Fluka, were used as a catalyst and initiator respectively. They were added into resin at 0.5% by weight of prepared resin. All chemicals were used as received without further purification.

The prepared resins were casted in silicone molds to obtain test specimens. The curing was done at 100°C for at least 48 h.

Testing of physical property

Tensile tests were carried out using a universal testing machine LLOYD LR 100 K at room temperature. Samples were made in accordance with ASTM D638-03. The flexural strength was determined according to ASTM D790-02 using a universal testing machine LLOYD L500. Impact properties of the samples were tested by ATS Charpy Impact Tester based on ASTM D6110-02. Hardness testing equipment was Durometer Shore D following the ASTM D2240-86. Thermal stability analysis was carried out with a Mettler Toledo thermal gravimetric analyzer (TGA) (Model TGA/SDTA 851) based on ASTM D3850. 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. According to ASTM D3418, Differential scanning calorimetry analysis (DSC) was performed using Netzsch DSC200 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).

RESULTS AND DISCUSSIONS

Unsaturated polyester resin preparation

The reaction mixtures were yellow liquid solution with fine white residues of titanium dioxide (TiO₂) commonly used as an additive in PET fiber production process. These residues can be simply removed by filtration. The viscosity of the glycolyzed products from the reactions carried out for 4, 6, and 8 h was 1616, 1456, and 1232 centipoise, respectively. The viscosity of glycolyzed products was reduced as the reaction time increased. This was owing to molecular chains that were getting smaller when the reaction

TABLE I
Yield and Hydroxyl Value of Glycolized Products

Glycolysis time	Yield (%)			HV (mg KOH/g)		
	PET fabric	T/C fabric	Soft-drink bottle	PET fabric	T/C fabric	Soft-drink bottle
4	61	55		217	187	
6	65	59		255	231	
8	71	62	76	298	269	322

time was prolonged. It was confirmed by the yield of the reaction and the HV of the glycolized products after free-glycol removal as shown in Table I. Although the yield increased slightly when the reaction time increased, the increase of HV was substantial as the number of the hydroxyl end groups increased. FTIR spectrum of the glycolized product is shown in Figure 1(a). Peaks corresponding to OH stretching, CH stretching, C=O stretching, C—O—C stretching, C—OH stretching and aromatic ester at wavenumbers of 3375, 2972, 1716, 1266, 1118, and 729 cm^{-1} , respectively, indicate the presence of compound or compounds having hydroxyl and ester groups.¹¹

The esterified products were viscous yellow to brown solution. In Figure 1(b), FTIR spectrum of

the esterified product shows peaks corresponding to para disubstituted aromatic ring, aromatic ring of styrene polymer, and aromatic ring of styrene monomer at wavenumbers of 876.87, 776.12 and 702.24 cm^{-1} , respectively. The esterified products from the glycolized products were successfully solidified by curing at 100°C for at least 48 h. As there was certain amount of free-glycol left in the glycolized products, it was reported that, at the end of esterification, not only different polymeric chains were produced by combination of the glycolized products with anhydrides but also unreacted oligomers and excess MA were present as impurities and formed the phase that is insoluble in styrene. This phase will not take part in crosslinking and hence the curing will be delayed.¹⁵

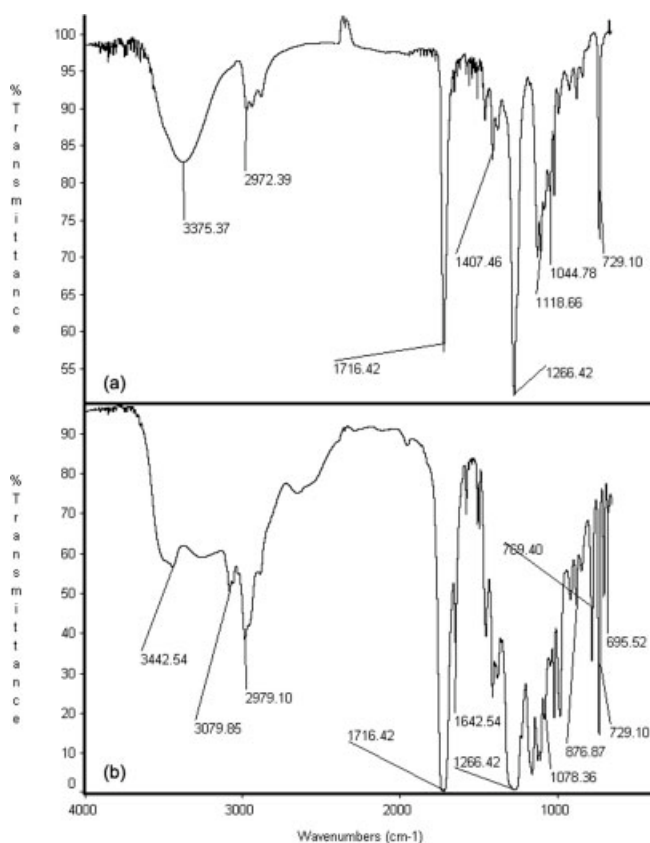


Figure 1 FTIR spectra of (a) the glycolized product from PET fabric and (b) the esterified product from the glycolized product.

Physical properties of cured resins

The tensile strength and modulus of cured resins are shown in Figures 2 and 3, respectively. These results suggested that the longer glycolysis time, the higher tensile strength, and modulus of cured resins were obtained. The viscosity and HV of the glycolized products after free-glycol removal suggested that, with longer glycolysis time, the products were composed of small oligomers rather than higher oligomers found in the glycolized products with less glycolysis time. This was in agreement with the finding report by Ghaemy and Mossaddegh.¹³ As a

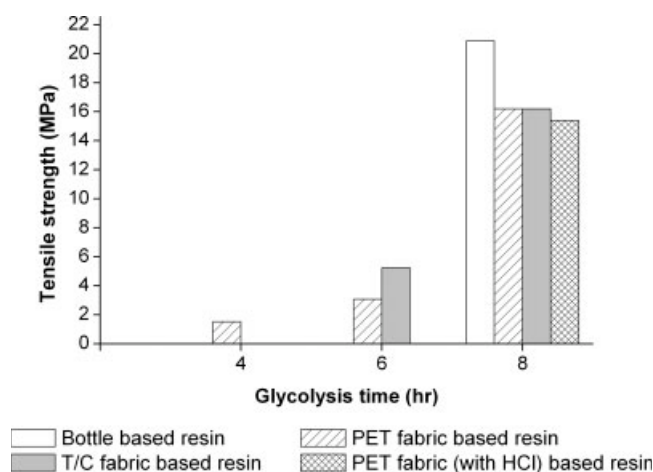


Figure 2 Tensile strength of cured resins.

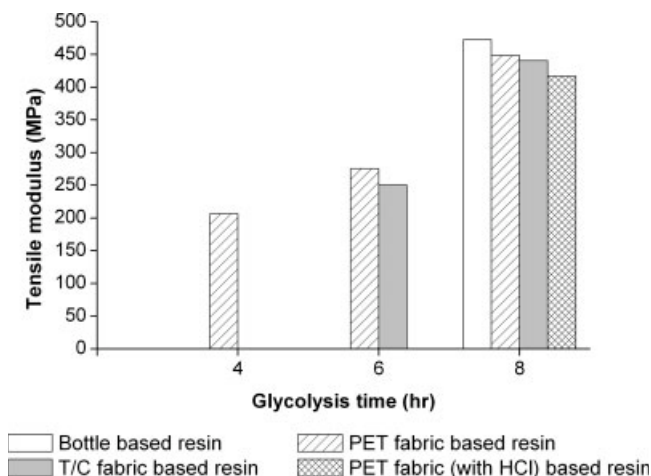


Figure 3 Tensile modulus of cured resins.

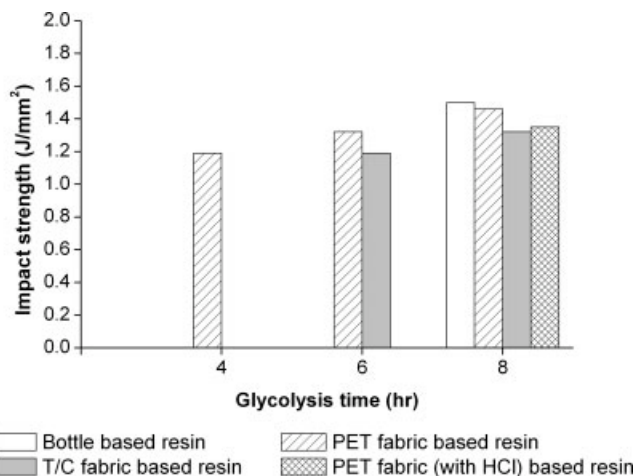


Figure 5 Impact strength of cured resins.

consequent, more hydroxyl terminal groups were found.⁴ For the reason that the oligomers obtained from the glycolysis were shorter, the distance between the curable double bonds decreased.¹⁷ Therefore cross-link density was presumably higher when the reaction was longer. Figure 4 shows the flexural strength of the cured resins. Similarly, as the glycolysis time increased, the flexural strength was increased. As a reference, samples were also prepared from the UPE resin prepared from glycolyzed soft-drink PET bottles. It was found that the tensile and flexural properties of the bottle based UPE resin were higher than those of the fabric based resins because of the differences in their molecular order.¹³ The yield as well as HV of the glycolyzed product from PET bottles was higher than those from fabrics. In Figures 5 and 6, similar trends also observed for the impact strength and the hardness. The impact strength and hardness of resin from 8-h glycolysis was highest when comparing with resin from 6- and 4-h glycolysis. As stated earlier, the

impurities formed as a separate phase may contribute to the lowered mechanical properties of the resins as well.

From these mechanical property results, it can be expressed that it is better to carry out glycolysis in a longer time as most of molecules were depolymerized into shorter segments providing higher degree of crosslinking. Shorter glycolysis time would give less monomer and dimer yields thus longer molecular chains as well as lower degree of crosslink, resulting in the inferior mechanical properties.¹³ However, glycolysis reaction time may not be over 8 h since the equilibrium of the glycolysis reaction is at 8 h.^{9,13} The above results also revealed that using HCl for elimination of cotton did not significantly affect the properties of the prepared resins.

From Figures 7–8 and Table II, it can be signified that the different in glycolysis times (8, 6, and 4 h) affected thermal stability of cured resins. The onset thermal degradation temperature (T_d) of the

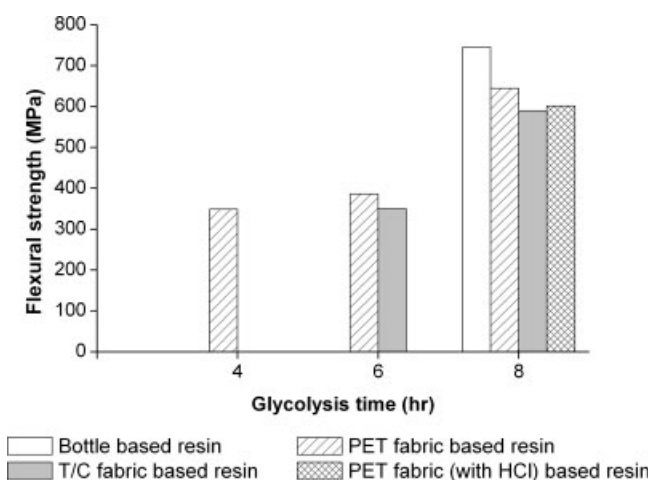


Figure 4 Flexural strength of cured resins.

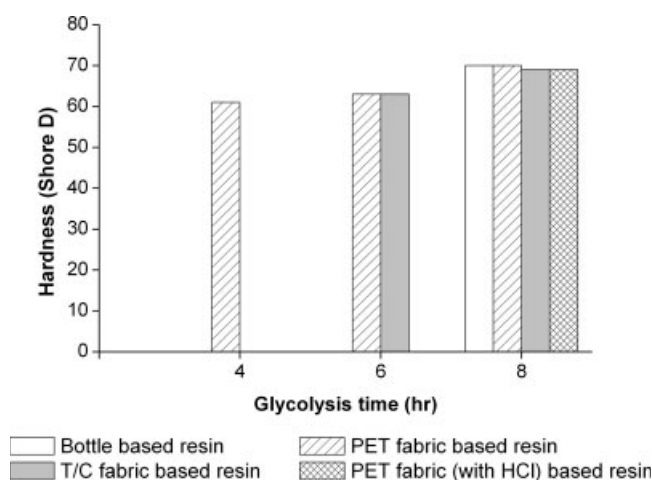


Figure 6 Hardness of cured resins.

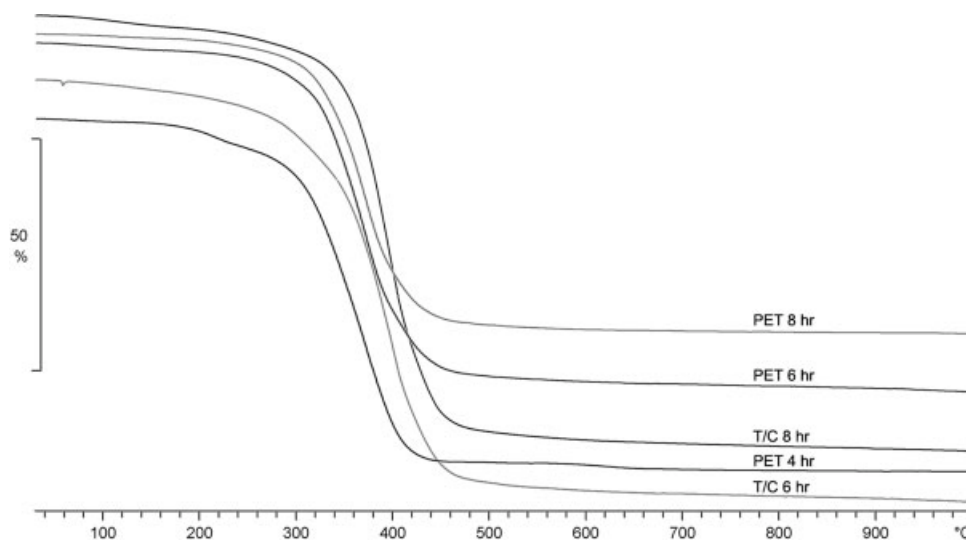


Figure 7 A TGA thermogram of PET and T/C fabrics based resins.

cured resins obtained from the 8-h glycolyzed product was the highest whereas one obtained from the 4-h glycolyzed product showed the lowest. A similar trend was found for the glass transition temperature (T_g). The more glycolysis time, the higher the T_g of the resins. As the glycolysis time increased, the smaller oligomers were obtained. As a consequence, more hydroxyl groups were found in the esterified products providing more crosslink sites in the resins. Because of the increasing amount of crosslinks increased, thermal stability of cured resins raised as the glycolysis reaction time increased.

CONCLUSIONS

UPE resins were successfully prepared from glycolyzed PET and T/C fabrics. PET and T/C fabrics were chemically recycled by glycolysis reaction resulting in smaller molecular chains. In the case of T/C fabric, the cotton was eliminated by dissolving in HCl prior to glycolysis. The extent of depolymerization was depended on the reaction time. It was found that when the reaction time increased, the molecular chains are shorter.

After esterification, unsaturated polyester resins were obtained. The resins were processed into test

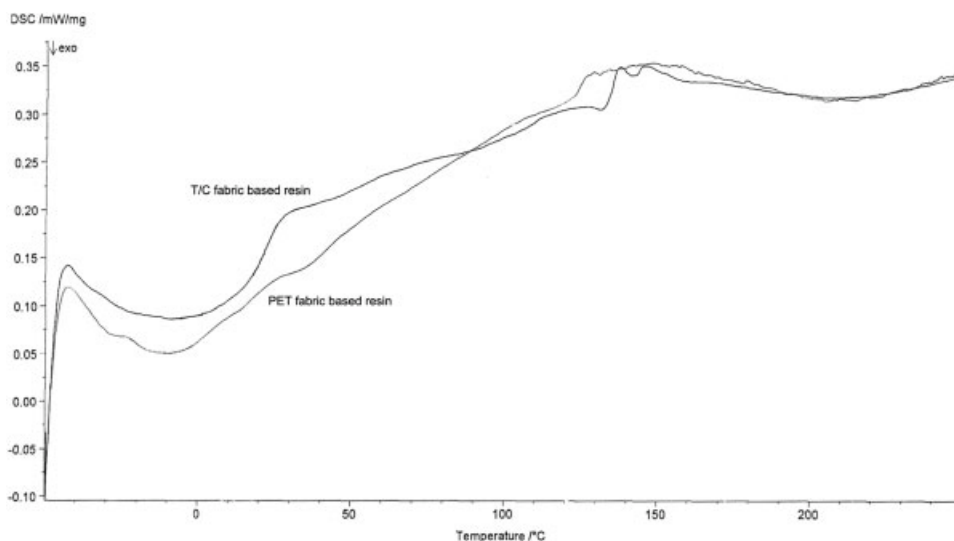


Figure 8 A DSC thermogram of PET and T/C fabrics based resins prepared from 8-h glycolyzed products.

TABLE II
Degradation Temperature and Glass Transition Temperature of Glycolyzed Products

Glycolysis time	Degradation temperature (°C)		Glass transition temperature (°C)	
	PET fabric based resins	T/C fabric based resins	PET fabric based resins	T/C fabric based resins
4	319		15	
6	335	327	19	20
8	345	371	23	22

specimens by casting and curing in silicone molds. The cured specimens were investigated for their mechanical properties those are tensile strength, tensile modulus, flexural strength, impact strength, and hardness. It was revealed that the mechanical properties of fabric based resins were slightly lower than those of the bottle based resin. Among the fabric based resins, the cured resin products prepared from the 8-h glycolyzed PET fabric possessed highest mechanical properties. Thermal degradation temperature and glass transition temperature, in agreement with mechanical properties, was higher in the case of cured resins obtained from the glycolyzed products obtained under longer reaction time.

References

- Margolis, J. M. *Engineering Thermoplastic-Properties and Application*; Princeton Polymer Laboratories: New Jersey, 1993.
- Scheirs, J. *Polymer Recycling*; Wiley: Sussex, 1998.
- Awaja, F.; Pavel, D. *Eur Polym Mater* 2005, 41, 1453.
- Paszun, D.; Spychaj, T. *Ind Eng Chem Res* 1997, 36, 1373.
- Nikles, D. E.; Farahat, M. S. *Macromol Mater Eng* 2005, 290, 13.
- Baliga, S.; Wong, W. T. J. *Polym Sci Part A: Polym Chem* 1989, 27, 2071.
- Vaidya, U. R.; Nadkarni, V. M. *J Appl Polym Sci* 1987, 34, 235.
- Vaidya, U. R.; Nadkarni, V. M. *Ind Eng Chem Res* 1987, 26, 194.
- Vaidya, U. R.; Nadkarni, V. M. *Ind Eng Chem Res* 1988, 27, 2056.
- Pimpan, V.; Sirisook, R.; Chuayjuljit, S. *J Appl Polym Sci* 2003, 88, 788.
- Saravari, O.; Vessabutr, B.; Pimpan, V. *J Appl Polym Sci* 2004, 92, 3040.
- Pardal, F.; Tersac, G. *Polym Degrad Stab* 2006, 91, 2567.
- Ghaemy, M.; Mossaddegh, K. *Polym Degrad Stab* 2005, 90, 570.
- Andreia Vasconcelos, A.; Cavaco-Paulo, A. *Cellulose* 2006, 13, 611.
- Aslan, S.; Immirzi, B.; Laurienzo, P.; Malinconico, M.; Martuscelli, E.; Volpe, M. G.; Pelino, M.; Savini, L. *J Mater Sci* 1997, 32, 2329.
- Öztürk, Y.; Güçlü, G. *Polym Plast Technol Eng* 2004, 43, 1539.
- Suh, D. J.; Park, O. O.; Yoon, K. H. *Polymer* 2000, 41, 461.