

Effect of Comonomers Composition on Tensile Properties of UV-Cured Acrylated Urethane-Oligoesters Derived from Poly (Ethylene Terephthalate) PET Waste.

Medhat S. Farahat Khedr*

Edward Waters University USA

*Corresponding Author

Medhat S. Farahat Khedr, Edward Waters University USA.

Submitted: 2023, June 29; Accepted: 2023, July 07; Published: 2023, July 19

Citation: Khedr, F. M. S. (2023). Effect of Comonomers Composition on Tensile Properties of UV-Cured Acrylated Urethane-Oligoesters Derived from Poly (Ethylene Terephthalate) PET Waste. *J App Mat Sci & Engg Res*, 7(2), 101-106.

Abstract

PET (polyethylene terephthalate) is a semicrystalline polymer which is characterized by its chemical resistance and bearing and wear properties. PET is often used for food processing machinery applications where low moisture absorption, low thermal expansion, resistance to staining, or resistance to cleaning chemicals is required. The chemical degradation process of PET waste by glycolysis reaction produces a potential starting material for many applications due to the chemical reactivity of their terminal hydroxyl groups that can be converted into various functional groups to produce versatile value-added products. Glycolyzed products of PET are oligoesters with terminal hydroxyl groups which can be modified into different reactive functional groups to produce linear and crosslinked polymers with excellent mechanical properties. The trend of utilizing the glycolyzed PET oligoesters in many applications provides a potential chemical route for recycling PET waste. In this study, PET was first depolymerized by glycolysis reaction and the obtained hydroxyl terminated oligoesters were reacted with half equivalent molar amount of toluene di-isocyanate TDI to convert it to hydroxyl terminated urethane-oligoester. The hydroxyl terminal groups were eventually modified into acrylate functional groups by acrylation reaction. The acrylated urethane-oligoesters were copolymerized with various acrylate, methacrylate and styrene monomers and cured by UV curing reaction and tested for their tensile properties. The measured tensile properties for samples in this work showed promising results for this new application of the glycolyzed products of PET waste.

Keywords: Polymer Recycling, Value-Added Products, Glycolysis of PET Waste, UV Curing, Tensile Properties, Acrylation Reaction, Urethane Oligoesters.

Introduction

PET has been a well-known packaging material for many decades and is considered the world's top choice for many foods and beverages because of its hygienic, high strength, light weight and shatter proofness. The highest application of PET lies in packaging carbonated soft drinks and water as a chemically safe material. The production of synthetic fibers from PET polymers fulfills more than half of the world's demand. PET was first synthesized in the United States by the mid-1940s when researchers were searching for an alternative synthetic material for natural textiles. Dacron is a branded synthetic polyester produced by DuPont. Furthermore, by the late 1950s, researchers managed to prepare stretched thin sheets of PET by extrusion molding to create films that are now extensively used as X-ray or photographic films. The technology of PET production and molding achieved much progress by the 1970s towards the formation of strong and light weight bottles. PET is highly resistant to attack by microorganisms or reaction with food products, and this privilege places it on top of packaging materials used in the processing of foods, beverages, and pharmaceuticals. Based on all these facts, health-safety agencies around the world

have approved PET as safe for use with foods and beverages for many decades. The massive production of polymeric packaging materials around the world has implemented research work for their recycling to manage their increasing waste volume. PET is on top of all recyclable polymer wastes due to the easiness of its chemical degradation by different methods, a fact that made it the most recycled plastic in the United States and worldwide. PET is recycled into shorter chain oligomers and co-reacted with different raw reactant materials with various functional groups to produce new polymeric materials or reproduce PET back and use it in different applications like automotive parts and construction materials. The endeavor of reducing the massive volume of discarded plastic products became mandatory for managing the growing portion of municipal solid waste (MSW) [1-2]. Statistical data revealed that the global production of PET increased from 41.56 million metric tons in 2014 to 73.39 million metric tons in 2020. The consumption of PET in the production of beverage bottles was recorded as 700 million pounds in 1987 in this industry alone[3]. PET can be depolymerized by different chemical methods due to the tendency of its ester functional groups to react

through nucleophilic addition reactions[4]. This reactivity towards nucleophilic addition reactions is due to the permanent polarity of ester linkages where the carbonyl C-atom carries a partial positive charge (+ δ) and the carbonyl O-atom has a partial negative charge (- δ). Nucleophilic reagents could be neutral or negatively charged. Neutral nucleophiles are Lewis bases in nature, examples include amines, alcohols, glycols, water, etc. (R-NH₂, R-OH, HO-R-OH, H₂O). Negatively charged nucleophiles are anions such as cyanides, chlorides, hydroxides, etc. (-CN⁻, Cl⁻, -OH⁻). This fact is the key point for many innovative depolymerization processes for converting PET waste into numerous value-added degradation products [5-11]. Examples for degradation of PET by neutral nucleophiles include hydrolysis (H₂O), aminolysis (R-NH₂), and glycolysis (HO-R-OH). Methanolysis has been evaluated as a method for recycling photographic and X-ray films, with more than 158 x 10⁶ kg converted since 1977[12]. However, large-scale degradation by methanolysis was not financially efficient [13]. For the purpose of highly efficient methanolysis, high-pressure reactors should be involved in the process [14-15]. Dupont et al [16-17]. reported on the degradation transesterification of PET scraps by 2-ethyl-1-hexanol for the purpose of synthesizing dioctyl terephthalate (DOTP) plasticizers for flexible PVC. PET waste can be used in molded or extruded articles after repalletizing [18]. However, repalletizing might degrade the polymer, adversely affecting its properties. Blending PET waste with raw polymer adversely affects the color and melt viscosity of the final product [19].

Current work aims first at degrading PET by glycolysis reaction and modifying the obtained oligoesters into UV curable oligomers through multiple step reactions to eventually produce new value-added products. The glycolysis process was carried out in the presence of manganese acetate as a transesterification catalyst at temperature range of 180-200 °C [20-23]. The produced polyols are used as reactive starting materials for other industries, such as polyurethanes PU[24], unsaturated polyesters [25-26] and modified unsaturated polyesters[27-30].

2. Experimental

2.1 Materials

Diethylene glycol C₄H₁₀O₃ (DEG), manganese(II) acetate Mn²⁺(CH₃COO)₂·2H₂O (Mn-ac), toluene diisocyanate C₉H₆N₂O₂ (TDI), acryloyl chloride C₃H₃ClO (ACL), 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-1-butanone C₂₃H₃₀N₂O₂ (BDMB) the photo initiator applied in the UV curing process, diethylene glycol diacrylate C₁₀H₁₄O₅ (DEGDA), diethylene glycol dimethacrylate C₁₂H₁₈O₅ (DEGDMA), triethylene glycol dimethacrylate C₁₄H₂₂O₆ (TEGDMA) and styrene C₈H₈ (Sty), were all purchased from Aldrich Chemical Co. and used without further purification.

Figure 1 shows the chemical structures for the monomers and chemicals applied in this work.

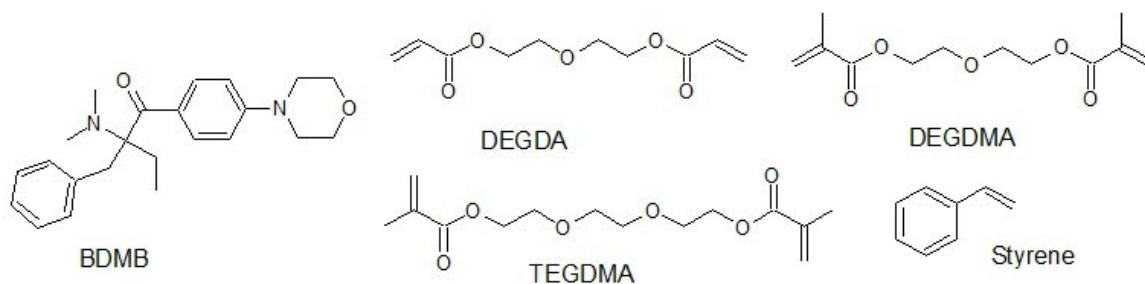


Figure 1: Chemical structures for the utilized monomers and photo initiator.

3. Results and Discussion

This work is a continuation of our previously published series of work on the modification of oligoesters derived from the glycolysis reaction of PET waste [27-30]. In our previous work, PET waste was depolymerized by DEG and the obtained oligoesters were reacted with half equivalent of TDI to insert a urethane moiety into the backbone of the oligoesters before modifying the terminal hydroxyl groups to acrylates. The hydroxyl terminal groups of the urethane-oligoesters were modified to acrylated urethane-oligoesters by acrylation

reaction[29-30]. The main goal of this work is to insert various functional groups and oligomer segments into the final chemical structure of this new UV curable oligomers to combine between different structural properties from each segment into the final cured polymers.

Figure 2 shows the chemical procedure steps of glycolysis of PET and chemical structural modifications to synthesize the modified acrylated urethane-oligoester GLYUA.

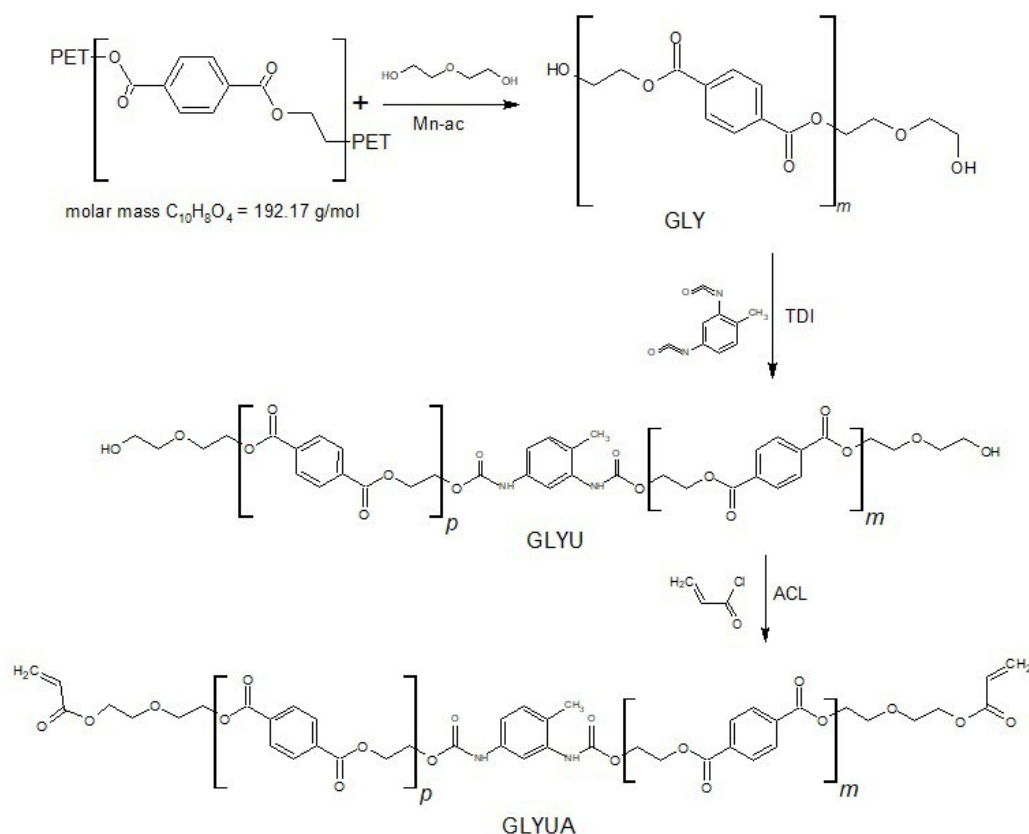


Figure 2: Chemical procedures for the synthesis of the acrylated urethane-oligoester GLYUA

3.1 Glycolysis of PET Waste to GLY Oligoesters

PET was first depolymerized by diethylene glycol DEG at the molar ratio of PET:DEG of 1:2.15 based on the molar mass of ethylene glycol terephthalate repeating unit $C_{10}H_8O_4$ (192.17 g/mol) and molar mass of DEG $C_4H_{10}O_3$ (106.12 g/mol). Depolymerization of PET was carried out in a continuously stirred three-necked flask equipped with a condenser, thermometer, and nitrogen inlet to avoid any undesirable oxidation side reactions in the presence of atmospheric oxygen at elevated temperatures. The temperature of the reaction was kept constant in the range of 180-200°C for a period of 4 hours[31-34]. After completion of glycolysis reaction, the product was cooled to room temperature and dissolved in an appropriate amount of dichloromethane DCM as a non-polar solvent for the glycolyzed product GLY and further purified by liquid-liquid chromatography LLC through phase separation using deionized water as a polar solvent to remove any unreacted glycol and catalyst [27-30]. The glycolyzed product GLY was collected and dried from DCM layer by a rotary evaporator and tested for acid number and hydroxyl value by End Group Analysis EGA.

3.2 Molecular Weight Determination by End Group Analysis EGA

The number average molecular weight $\langle M_n \rangle$ of the obtained GLY was calculated according to end group analysis method by determining the acid number (A) and hydroxyl value (B) (mg KOH/g sample) and substitution into Equation (1) [35-40]. Where n refers to the number of hydroxyl terminal groups per oligoester molecule.

$$M_n = (n \times 56.1 \times 1000) / (A+B) \quad (1)$$

3.3 Molecular Weight Determination by Gel Permeation Chromatography (GPC)

GPC analyses were performed on SEC Inst., using THF as a solvent at ambient temperature. For measurement, a 20 μ L sample was injected at a flow rate of 1 mL/min. using Waters 5/5 HPLC pump. Two successive columns (PSS SDV linear XL 5 μ , 8x600 mm) and (PSS SDV 100 A° 5 μ , 8x600 mm) and (PSS SDV 100 A° 5 μ , 8x600 mm) were applied. Detection was performed on a Waters 410 Differential Refractometer using a linear UVIS-205 absorbance detector. The structure of the obtained GLY oligoesters showed that the number of terminal hydroxyl groups per oligoester molecules ($n = 3$) and the measured $\langle M_n \rangle$ from EGA and GPC lied between 480-500 (g/mole)[27-30]

3.4 Synthesis of Urethane-Oligoesters GLYU

The purified and dried GLY was reacted with half equivalent of TDI based on the determined hydroxyl value(B) by EGA method to form a hydroxyl terminated urethane-oligoester GLYU. Reaction with TDI was carried out by heating at 70 °C inside a vacuum oven for 12 hours to ensure complete reaction of cyanate groups with equivalent hydroxyl groups. The remaining unreacted terminal hydroxyl groups of GLYU were modified into acrylate groups through acrylation reaction to prepare the target acrylated urethane-oligoester GLYUA[29-30].

3.5 Synthesis of the Acrylated Urethane-Oligoester GLYUA

The terminal hydroxyl groups of the urethane-oligoester GLYU were converted to acrylate groups by acrylation reaction

according to the published methods [33-34]. A 250 mL round-bottom three-necked flask equipped with a magnetic stirrer and a nitrogen sparge tube was charged with 150 mL tetrahydrofuran (THF), x mol of purified GLYU and 3x mol triethylamine. After cooling the mixture under a nitrogen spurge to 0 °C with an ice bath, the calculated equivalent moles of acryloyl chloride were added dropwise through addition funnel over a period of 30 minutes. The mixture was kept at 0 °C for 3 h and allowed to reach room temperature and remain for an additional 3 h. After filtration and removal of the THF under vacuum, the crude product was dissolved in DCM. The DCM layer was washed out with 1.0 M aqueous NaOH and saturated aqueous NaCl, three times in each case, followed by drying the organic layer over anhydrous Na₂SO₄. The collected GLYUA in DCM layer was further purified by passage over an anhydrous silica gel column using a CH₃OH/CH₂Cl₂ (50:50 v/v) mixture as a mobile phase [41-42]. DCM was evaporated from GLYUA by rotary evaporator and cured solely and by copolymerization with UV curable monomers using UV curing method and tested for Young's modulus, % elongation and break strength.

3.6 UV Curing

GLYUA was polymerized solely as a control sample for comparison with other samples in which it was copolymerized with different UV curable monomers like DEGDA, DEGDMA, TEGDMA and styrene where all ingredients were added on the basis of weight ratios. Polymerization and crosslinking

reactions were carried out under UV irradiation using 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-1-butanone BDMB as a photo initiator and the cured films were tested for tensile properties. UV Curing step was carried out by using 2 wt.-% BDMB and UV irradiation at $\lambda = 254$ nm at an output intensity of 400 W/inch. The speed of the conveyor belt was 5 ft/min for a traveled distance of $l = 33.0$ inches. Cured films were obtained by casting liquid comonomer mixtures plus photo initiator onto glass plates using steel thickness guard adjusted at thickness of 4 mils (0.102 mm).

3.7 Tensile Properties of the UV Cured Samples.

Tensile properties of the cured films were reported in terms of Young's modulus (E GPa), tensile strength at break (TS MPa) and percent elongation at break (% E). Young's modulus E is a measure of the maximum resistance of a material to elastic (recoverable) deformation under loading where beyond that point the material changes to plastic (non-recoverable) deformation. Stiff materials exhibit high values of E and change their shapes very slightly under the applied loads. Whereas rubbery and flexible materials show low values of E and change their shapes considerably under the applied loads. Young's modulus E is equal to elastic stress/strain and has the same units of stress, N/m², or Pascals (1 Pa = 1 N/m²; 1 MPa = 10⁶ Pa, 1 GPa = 10⁹ Pa). Tensile properties of the UV cured samples are presented on Table 1 [43-45].

Sample code	GLYUA Wt%	DEGDA Wt%	DEGDMA Wt%	TEGDMA Wt%	Styrene Wt%	Young's Modulus (E) GPa	Tensile strength at break (TS) (MPa)	% Elongation at break (%)
PU-1	100.0	-	-	-	-	1.5	7.3	4.3
PU-2	50.0	50.0	-	-	-	2.0	36.0	2.2
PU-2-sty	50.0	25.0	-	-	25.0	1.7	37.2	3.8
PU-3	50.0	-	50.0	-	-	2.1	15.0	0.8
PU-3-sty	50.0	-	25.0	-	25.0	2.0	25.2	1.3
PU-4	50.0	-	-	50.0	-	2.6	30.5	1.2
PU-4-sty	50.0	-	-	25.0	25.0	2.4	49.0	2.7

Table 1. Tensile properties of the UV cured samples.

The measured values of E for the UV-cured samples lied between 1.5 to 2.6 GPa which matched those for commercial polymers like cellulose acetate, epoxy resins, acrylonitrile-styrene-butadiene ABS, polyvinylchloride PVC and Nylons with the advantage of showing about tenfold higher tensile strength TS over them [46]. It is well known that value of E increases as the crystallinity of the cured polymers increases. Also, the tensile strength TS increases by increasing the crosslink density between linear chains. PU-1 was used as the control sample where GLYUA was cured solely, and other samples were prepared by copolymerization with other monomers at different weight percentages. Mechanical properties for the cured PU-1 showed that it is the least stiff sample as indicated by its low modulus E (1.5 GPa) and low tensile strength TS (7.3 MPa). Exploring the results on table 1 shows that copolymerization of GLYUA with DEGDA and DEGDMA increased the stiffness of samples as indicated by the increase in the values of E by 0.5-0.6 GPa whereas copolymerization with TEGDMA pronouncedly increased the modulus E by 1.1 GPa. This can be attributed to

the increased crystallinity exhibited by TEGDMA segments because of their longer monomer chain compared with those of DEGDA and DEGDMA. Incorporation of 25% wt./wt. styrene monomer slightly decreased the value of E in all samples and this might be due to the increase of the amorphous segments of the final cured structure but at the same time it increased their tensile strength TS which can be attributed to the increased crosslink density. In reference to our previous work, recent results showed recognizable improvement in the mechanical properties of the UV cured samples due to modification of the chemical structure by incorporation of TDA in the backbone of GLYUA and due to copolymerization with styrene [29-30].

4. Conclusion

Chemical degradation of PET waste by glycolysis reaction into polyol oligoesters represents an important endeavor for polymer recycling and creating innovative value-added products. Steps of modification of these polyol oligoesters were achieved by inserting urethane nucleus into the chemical structure of the

glycolized products by reaction with TDI and modifying the terminal hydroxyl groups into UV curable acrylate groups as presented by the control sample GLYUA. The mechanical properties of the cured samples were noticeably improved by copolymerization with 50% DEGDA, DEGDMA and TEGDMA and further improved in terms of tensile strength at break TS by incorporation of 25% by weight of styrene monomer.

Acknowledgement

This research work was carried out at the University of Alabama, chemistry department under a project funded by the U. S. Environmental Protection Agency under grants R826728 and R827121. The contents do not necessarily reflect the views and policies of the U.S. EPA, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use. The author cordially expresses his gratitude and acknowledgement for the continuous research support and help offered by Professor Dave E. Nikles and the staff at the center for materials for information technology at the University of Alabama.

Data Availability

The data sets generated and analyzed during the current study are available at the following journals online repository, Macromolecular Materials and Engineering MME and Polymer International PI.

[https://doi.org/10.1002/14392054\(20011101\)286:11<695::](https://doi.org/10.1002/14392054(20011101)286:11<695::AID-MAME695>3.0.CO;2-V)

[AID-MAME695>3.0.CO;2-V](https://doi.org/10.1002/1439-2054(20020501)287:5<353::AID-MAME353>3.0.CO;2-H)

[https://doi.org/10.1002/1439-2054\(20020501\)287:5<353::AID-](https://doi.org/10.1002/1439-2054(20020501)287:5<353::AID-MAME353>3.0.CO;2-H)

[MAME353>3.0.CO;2-H](https://doi.org/10.1002/pi.818)

<https://doi.org/10.1002/pi.818>

References

- Liptak, B. G. (1991). Municipal waste disposal in the 1990s. CRC Press.
- Rhyner, C. R., Schwartz, L. J., Wenger, R. B., & Kohrell, M. G. (2017). Waste management and resource recovery. CRC Press.
- Bledzki, A. K., (1997). "Recycling of Polymer Material", WNT, Warsaw
- Long, T. E., & Scheirs, J. (Eds.). (2005). Modern polyesters: chemistry and technology of polyesters and copolyesters. John Wiley & Sons.
- Mleziva, J., Sofia, T. (1969). "Polyesters"
- Petuhov, B. V., Moscow, K. (1976). Polyester Fibers, 81-181.
- Todorov, K., K. Kolev, I. Iranov, A. Todorova and A. Georgieva, Bulgarian Authorship Certificate No. 47724 (1989).
- Neale, C. W., Hilyard, N. C., & Barber, P. (1983). Observations on the economics of recycling industrial scrap plastic in new products. Conservation & recycling, 6(3), 91-105.
- Jensen, J. W., Holman, J. L., & Stephenson, J. B. (1974). Recycling and disposal of waste plastics. Ann Arbor Science.
- J. Milgrom, "Polyethylene terephthalate. In Plastics Recycling", Ehrig, RJ (ed.), Hanser Publisher; Munich (1989).
- Warren, L. M., & Burns, R. (1988). Processors make a go of mixed-waste recycling. Plast. Technol., 34(6), 41-42.
- Van, H. (1990). Kodak begins recycling film. Chem. Mark. Rep, 237.
- R. Martino. (1990). Modern Plastics, 126.
- U.S. Pat. 3, 037, 048 (1962), inv.: R. Lotz.
- U.S. Pat. 4, 578, 502 (1962), inv.: W. J. G. Cudmore.
- Dupont, L. A., & Gupta, V. P. (1993). Degradative transesterification of terephthalate polyesters to obtain DOTP plasticizer for flexible PVC. Journal of Vinyl Technology, 15(2), 100-104.5.
- U.S. Pat. 5, 101, 064 (1992), invs.: L. A. Dupont and V. P. Gupta.
- U. S. Pat. 4, 164, 880 (1979), invs.: W. H. Cobbs, M. J. Stewart.
- 7 Sitting, M. (1981). Organic and polymer waste reclaiming encyclopedia.
- Chen, J. W., & Chen, L. W. (1999). The glycolysis of poly (ethylene terephthalate). Journal of Applied Polymer Science, 73(1), 35-40.
- Hubert, F., Durand, G., & Tersac, G. (1999). Equilibria in the alcoholysis reactions of terephthalic esters and chemical valorization of polyethyleneterephthalate waste. I. Equilibrium constants determination. Journal of applied polymer science, 72(3), 329-340.
- Halacheva, N., & Novakov, P. (1995). Preparation of oligoester diols by alcoholic destruction of poly (ethylene terephthalate). Polymer, 36(4), 867-874.
- Baliga, S., & Wong, W. T. (1989). Depolymerization of poly (ethylene terephthalate) recycled from post-consumer soft-drink bottles. Journal of Polymer Science Part A: Polymer Chemistry, 27(6), 2071-2082.
- U. R. Vaidya and V. M. Nadkarni, J. Appl. Polym. Sci., 1988, 35, 775.
- Vaidya, U, R. Nadkarni, V, M. (1988). Ind. Eng. Chem. Res. 26, 194.
- Vaidya, U, R. Nadkarni, V, M. (1988) Unsaturated polyester resins from poly (ethylene terephthalate) waste. 2. Mechanical and dynamic mechanical properties Industrial & Engineering Chemistry Research, 27 (11). pp. 2056-2060
- Farahat, M, S. Abdel-Azim A, A and Abdel-Raowf, M, E. (2000) Modified unsaturated polyester resins synthesized from poly(ethylene terephthalate) waste, 1. Synthesis and curing characteristics 283, 1.
- M. S. Farahat, Polym. Int., 2002, 51, 183.
- M. S. Farahat and D. E. Nikles, Macromol. Mater. Eng., 2001, 286, 695
- M. S. Farahat and D. E. Nikles, Macromol. Mater. Eng., 2002, 287, 353
- Tong, S. N., Chen, D. S., Chen, C. C., & Chung, L. Z. (1983). Unsaturated polyesters based on bis (2-hydroxyethyl) terephthalate. Polymer, 24(4), 469-472.
- Rebeiz, K. S., Fowler, D. W., & Paul, D. R. (1992). Polymer concrete and polymer mortar using resins based on recycled poly (ethylene terephthalate). Journal of applied polymer science, 44(9), 1649-1655.
- Ali, S., Cuchiara, M. L., & West, J. L. (2014). Micropatterning of poly (ethylene glycol) diacrylate hydrogels. In Methods

- in Cell Biology (Vol. 121, pp. 105-119). Academic Press.
34. Ahn, K. D., Chung, C. M., & Kim, Y. H. (1999). Synthesis and photopolymerization of multifunctional methacrylates derived from Bis-GMA for dental applications. *Journal of applied polymer science*, 71(12), 2033-2037.
35. Siggia, S., & Hanna, J. G. (1963). Quantitative organic analysis via functional groups. (No Title).
36. Stetzler, R. S., & Smullin, C. F. (1962). Determination of Hydroxyl Number of Polyoxyalkylene Ethers by Acid-Catalyzed Acetylation. *Analytical Chemistry*, 34(2), 194-195.
37. Fritz, J. S., & Schenk, G. H. (1959). Acid-catalyzed acetylation of organic hydroxyl groups. *Analytical Chemistry*, 31(11), 1808-1812.
38. Fritz, D. F., Sahil, A., Keller, H. P., & Kovats, E. (1979). Determination of hydroxyl groups in poly (ethylene glycols). *Analytical Chemistry*, 51(1), 7-12.
39. Sorenson, W. R., & Campbell, T. W. (2001). Preparative methods of polymer chemistry. (No Title).
40. Odian, G. (1981). *Principles of Polymerization*, 2ndEdn. Wiley-Interscience: New York, 204, 243-249.
41. Priola, A., Gozzelino, G., Ferrero, F., & Malucelli, G. (1993). Properties of polymeric films obtained from uv cured poly (ethylene glycol) diacrylates. *Polymer*, 34(17), 3653-3657.
42. G. Malucelli, G. Gozzelino, R. Bongiovanni and A. Priola, *Polymer*, 37, 2565.
43. ASTM International. (2014). Standard test method for tensile properties of plastics. ASTM international.
44. ASTM D882 - Standard Test Method for Tensile Properties of Thin Plastic Sheeting
45. ASTM E111 - Standard Test Method for Young's Modulus, Tangent Modulus, and Chord Modulus
46. D. W. Van Krevelen and K. Te Nijenhuis, *Properties of Polymers*, 4th ed., 2009, chapter 13.

Copyright: ©2023 Medhat S. Farahat Khedr. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.