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Synthesis and Evaluation of Urethane Polymers from PET Waste

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Abstract

This study is engaged in synthesis of novel monomer bis(2-hydroxyethyl) by chemical recycling of PET waste using excess of thioglycol in prescience of (0.5%) zinc acetate as catalyst. Best yield of monomer was obtained (40%) when using 1:6 PET to thioglygol molar ratio and 16 hours reaction time. The thiolyzed products were purified and characterized by FTIR, ^{1}H NMR and CHNS analysis and these characterizations were proved that nucleophilic attack to carbonyl groups of PET backbone was achieved by thiol groups instead of hydroxyl groups of thioglycol. Also, urethane polymers were prepared by reaction of various weight ratios of bis(2-hydroxyethyl) thioterephthalate-poly(ethylene glycol) mixtures with 2,4-toluene diisocyanate monomer. Good mechanical compression of polyurethane polymers were obtained and evaluated showing transition properties from rigid to flexible urethane polymers.

Introduction

Poly(ethylene terephthalate) (PET) is a thermoplastic polyester showing excellent thermal and mechanical properties. PET is one of the versatile engineering plastics, which is used to manufacture mainly textiles and bottles, as well as packaging, photographic films, video and audio tapes *[1]*. Large numbers of post-consumer PET products, especially bottles and containers, do not create a direct hazard to the environment, but are being concerned due to their substantial volume fraction in the solid waste streams, their high resistance to the atmosphere, their poor biodegradability and photo degradability. Recently, recycling of PET by both ways chemical and physical recycling has received a great deal of attention and many attempts are currently directed toward recycling of post-consumer PET products because of both environmental protection and economic benefits *[2]*.

Currently, the dominant form of PET recycling worldwide is physical recycling. Physical recycling is few mechanical and thermal steps contains grinding PET bottles into powder. The general process of physical recycling involves a six-stage process: sorting, granulation, flotation, washing, drying, and extrusion *[3]*. Because PET is degraded using physical means, the powder gathered from physical recycling does not share the same quality properties as virgin PET. Scheirs [4] reported that cyclic and linear oligomeric compounds are formed during the physical reprocessing of PET as a due to thermal degradation reactions. He also showed that the oligomer content increases in recycled PET. Therefore, physically recycled PET cannot be reused in plastic bottle production due to the diminished mechanical properties of PET through physical degradation *[5]*. Instead, these recycled products have been commercially produced to be use as fibers in variety of secondary applications varying from clothing to carpeting *[6]*.

On the other side, chemical recycling has received a great attention because this kind of recycling does not only serve as a partial solution to the solid-waste problem, but also serve as a source of raw material of some industries, i.e., new monomers and oligomers obtained from PET recycled *[7]*. Chemical recycling of PET includes chemolysis of the polyester with an excess of reactants so it can be carried out in many ways such as glycolysis, methanolysis, hydrolysis, aminolysis, ammonolysis and similar processes. Ethylene glycol (EG) and bis(2-hydroxyethyl) terephthalate (BHET) are monomers obtained by glycolysis of PET under excess of ethylene glycol in presence of zinc acetate as catalyst *[11-8]*.

Many researchers reported that the products obtained from depolymerization of PET used in various applications such as epoxy *[12]*, Alkyd Resins *[10]*, aromatic polyester *[13]*, unsaturated polyester *[14]*, biodegradable polyurethane *[15]*, surface coating material [16]. These applications provide an economical flexibility when using the raw recycled monomer for the most profitable option upon demand.

Materials and instruments

PET flakes were obtained from clear-transparent soft drink bottles. The PET bottles label were removed and then, bottles were cut in to small pieces, washed and dried. Other chemical materials are thioglycol (2-mercaptoethanol), zinc acetate, poly(ethylene glycol) M.Wt = 400 g/mole, 2,4-toluene diisocyanate, triethylamine and 2,4-toluene diisocyanate were obtained from Fluka, which were used without purification . JASCO FTIR 4200 instrument was used to characterize the reactant materials and thiolyzed products. While, The ^{1}H NMR spectrum of thioglycol and thiolyzed products was also recorded by BRUKER 400 MHz instrument at frequency 250 MHz in DMSO as a solvent. The weight of elements (C, H and S) for BHETT monomer was instrumentally analyzed by CHNS-O Pokin Elemer 2400-II, it was needed to record this analysis 1.5520 mg of BHETT and 970-70 ^{0}C with 100 ml/min flow rate. The compression tester, Zwick Roell BT1-FR2.5TH.D14 instrument, was used to evaluate mechanical compression properties of foam specimens.

Methods

A. *Synthesis of thiolysed products*

Solid PET wastes was thiolysed by thioglycol, different mole ratios (1:2, 1:4, 1:6 & 1:8) of PET to thioglycol were charged in three-neck round bottom flask, which was fitted with stirrer, reflex condenser and thermometer in presence of (0.5%) zinc acetate as catalyst. The mixture was heated to reflex for (4, 8, 16 & 24 hours) and cooled to room temperature. Next, distilled water was added to the residual solid. The mixture was heated to boil and filtered directly to separate monomer from oligomer and unreactant PET. The filtered monomer was cooled to room temperature and then keep to 4 ^{0}C for four days. White crystal was filtered and purified by recrystallization by hot water. Methylene chloride was used to isolate oligomer from residual PET. Both monomer and oligomer were dried at 40 ^{0}C for 48 hour and characterized by FTIR, ^{1}H NMR and CHNS analysis.

B. *Preparation of urethane polymers*

Various mole ratios of bis(2-hydroxyethyl) thioterephalate (BHETT) were well-mixed with viscos liquid of poly(ethylene glycol) (PEG), as shown in table-1. The hydroxyl number and number average molecular weight of diol mixture was determined by end hydroxyl group analysis *[17]*. Then, one drop of trimethylamine (TEA) was added as catalyst to diol mixture. The polyurethane was prepared by reacting directly of 1 mole of 2,4-toluene diisocyante (TDA) and 1 mole of diol mixture at the room temperature for 24 hour, and the temperature was 50 ^{0}C for 12 hour, to ensure react mostly residual hydroxyl and isocyante groups in polymer foam to form urethane linkage. Finally, foam was cut as cubic shapes with same diameter, 10 cm for each side, to evaluate their mechanical compression.

Table-1: Weight ratios and hydroxyl values of diol mixture (PEG and BHETT)

Specimens name	***BHETT Weighs (%) with diol mixture***	***PEG Weigh (%) with diol mixture***	***Density [g/dm]***	***M.Wt [g/mol] of diol mixture***
S1	0	100	64	405
S2	10	90	65	391
S3	20	80	62	379
S4	30	70	66	364
S5	40	60	67	355
S6	50	50	65	340
S7	60	40	61	329
S8	70	30	68	317
S9	80	20	65	306
S10	90	10	65	293
S11	100	0	70	286

Results and discussion

A. The influence of reaction conditions on thiolyzed products

Thiolysis of PET is depolymerization processes that full to partial decomposition of PET chains were achieved by nucleophilic attack of the thiol groups to the ester linkages extending along polymer backbone chains at certain conditions, and the ester linkages cleavage by thioesterification mechanism *[18]*. In this work, bis(hydroxyethyl) thioterephthalate (BHETT) is a monomer which was obtained by full thiolysis decomposition of PET waste using excess of thioglycol in presence of 0.5% zinc acetate. The following reaction, scheme-1, shows the depolymerization mechanism of this PET. The PET to thioglycol molar ratio and reaction time are important factors that must be considered in order to obtain higher yield. So that, reaction was carried out at the same time (8 hour) and same amount of catalyst but different PET to thioglycol molar ratio (1:2, 1:4, 1:6 & 1:8), shown as in Figure-1. Then, the reaction was repeated at different reaction time (4, 8, 16, 24) by fixing the mole ratio of the reactants as shows in Figure-2.

The results in Figure-1 and Figure-2 show that 1:6 mole ratio of PET to thioglycol and 16 hours provide the higher yield percentage of the product, therefore the reaction was carried out under these conditions.

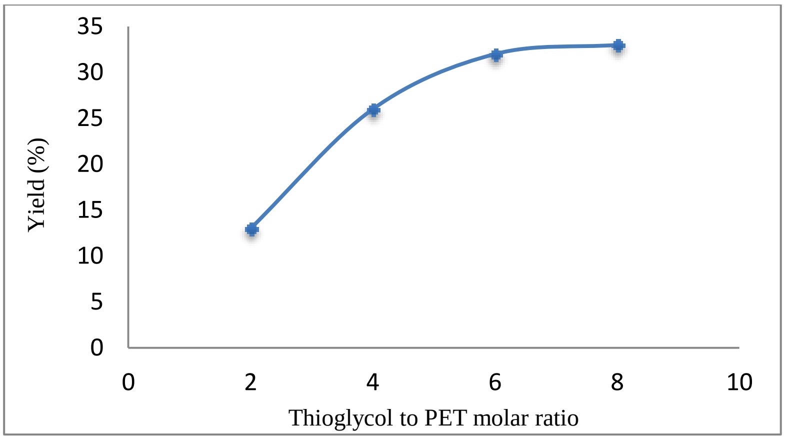


Figure-1: Effect of BBHET yield with PET to thioglycol molar ratio for 8 hour.

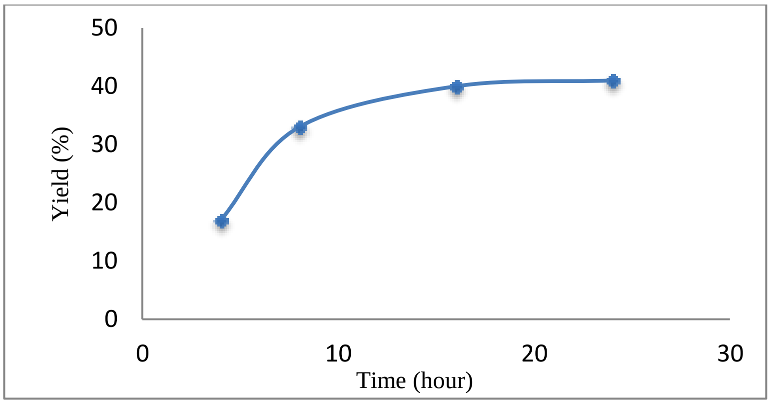
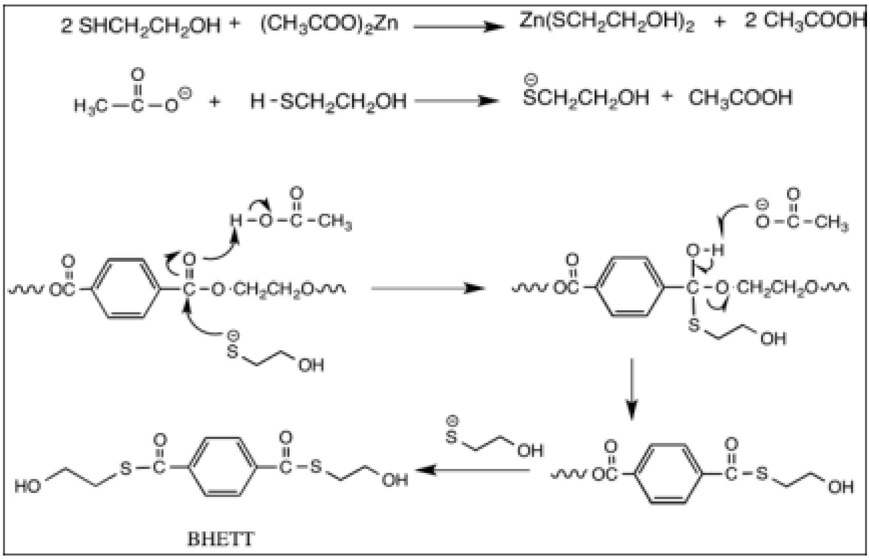


Figure-2: Effect of BBHET yield with reaction time (1:6 PET to thioglycol molar ratio).



Scheme-1: Thiolysis mechanism of PET with thioglycol

B. Characterization of thiolyzed PET

- FTIR analysis

The FTIR spectrum of thioglycol, as shown in Figure-3, indicates the appearance of hydroxyl group as broad peak at 3600-3200 cm^{-1}, and a peak at 2555 cm^{-1} is for S-H bond for thiol group. Figure-4 shows FTIR spectrum of PET that has a sharp and strong peak at 1720 cm^{-1} related to starching of aromatic carbonyl-ester double bonds along the polymer backbone chains. Other peaks at 2920-2870 cm^{-1} and 3100-3000 cm^{-1} represent to aliphatic and aromatic C-H bonds respectively. Degradation of PET chain produces thioester groups instead of ester groups, which starch at wave number 1670-1695 cm^{-1} *[19]*. appearance a broad band at 3600-3200 cm^{-1} for free hydroxyl group and a band at 1690cm^{-1} for thioester with disappearance the band at 1720 cm^{-1} for carboxylic ester and band at 2555 cm^{-1} for thiol groups confirm that the nucleophilic attack was proceeded by thiol groups instead of hydroxyl group of the thioglycol agent, as shown in Figure-5. Oligomer also shows in Figure-6, and important wave number bands show in table-2.

Table-2: IR absorption bands (cm-1) of compounds, oligomer and polymer

υ St. (cm^{-1}) / ***materials***	***O–H***	***S–H***	***(C=O) Ester***	***(C=O) Thioester***
PET	-	-	1720	-
Thioglycol	3650-3100	2555	-	-
BHETT	3600-3150	-	-	1690
Oligomer	3650-3200	-	1716	1690

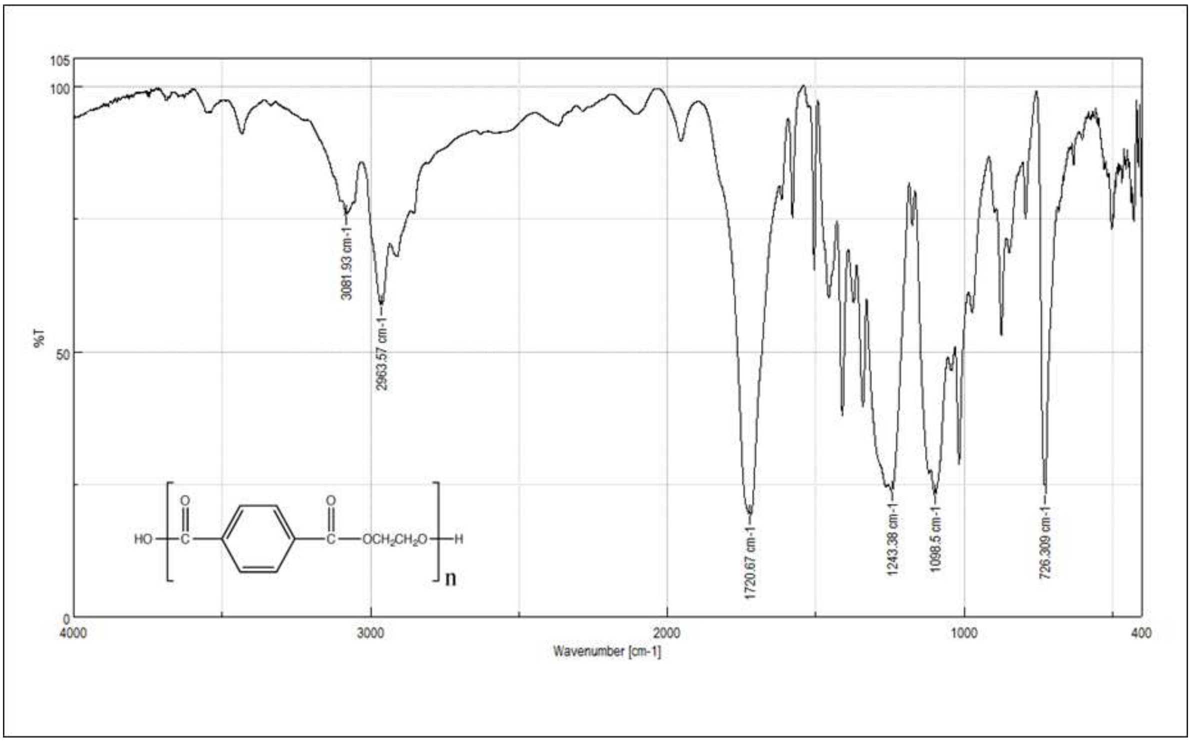


Figure-3: FTIR spectra of PET waste.

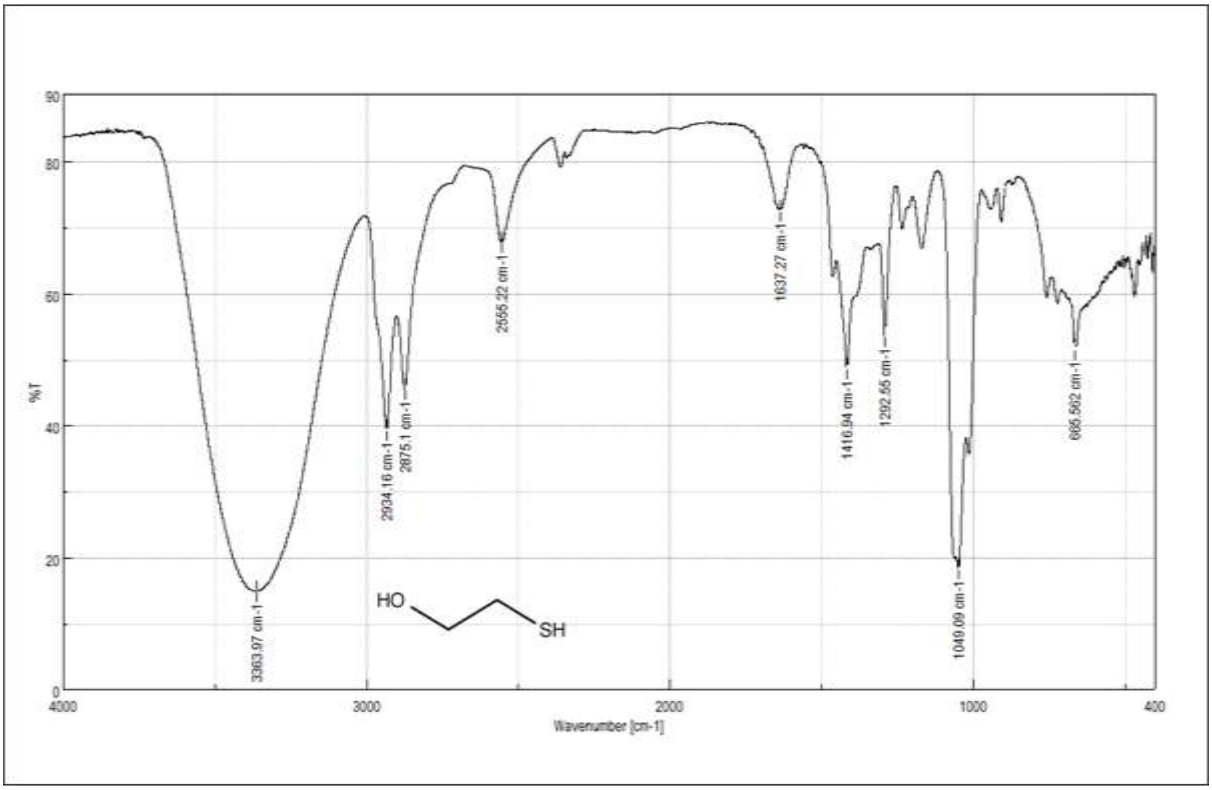


Figure-4: FTIR spectra of thioglycol monomer.

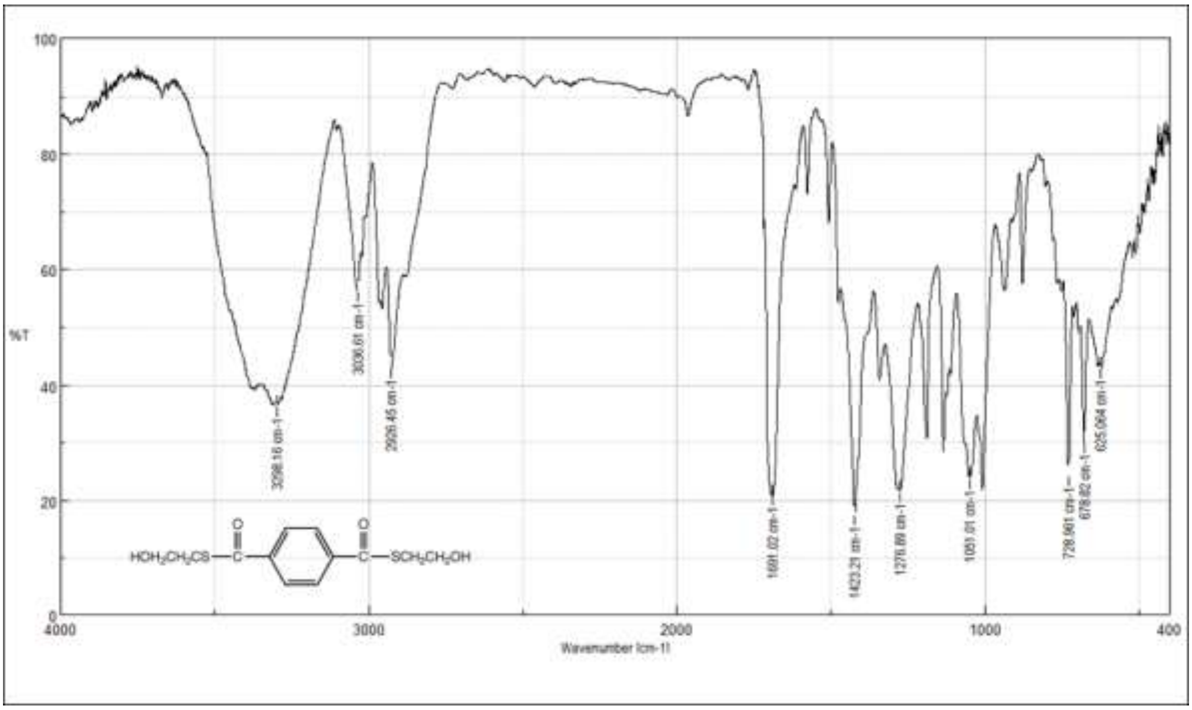


Figure-5: FTIR spectra of BHETT of thiolyzed products (PET to thioglycol mole ratio is 1:6).

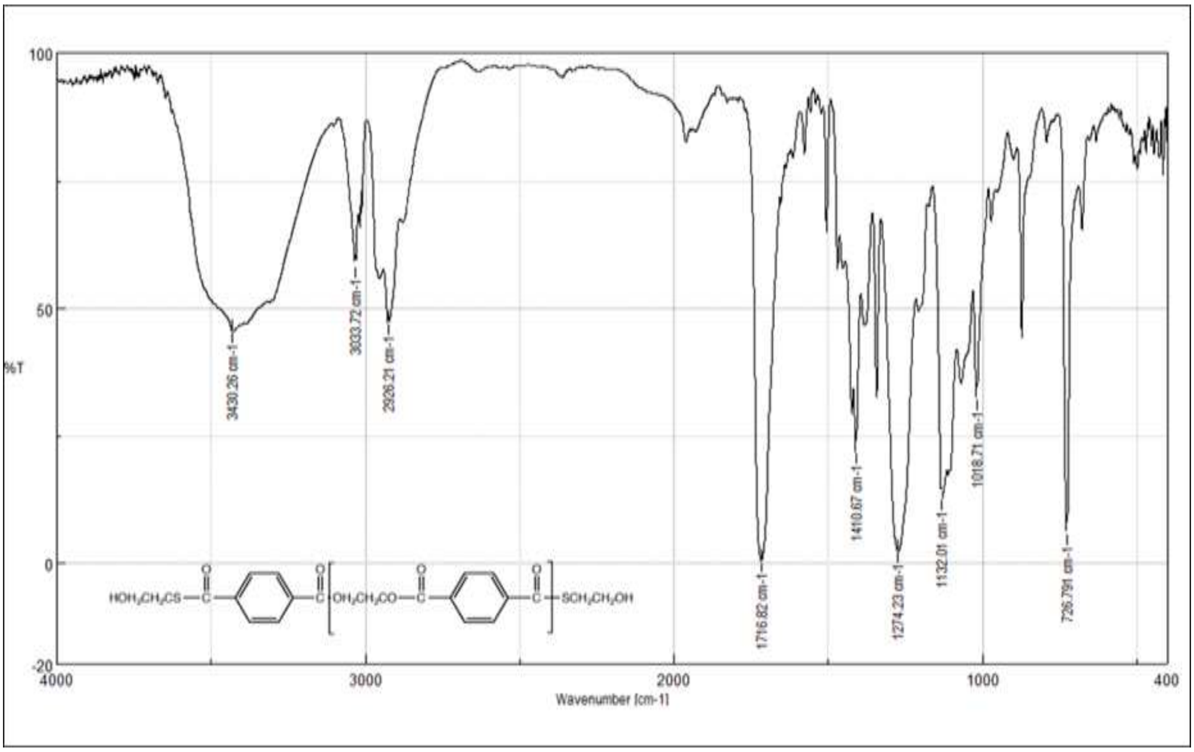


Figure-6: FTIR spectra of oligomer of thiolyzed products (PET to thioglycol mole ratio is 1:6).

- ^{1}H NMR analysis

The ^{1}H NMR of thioglycol shows in Figure-7. The compound was characterized by four groups; thiol group SH which appear as triplet signal at 1.936 ppm, aliphatic group CH_2 that neighboring thiol group which appears as quartet signal at 2.414 ppm, aliphatic group CH_2 that neighboring to alcoholic group which has triplet signal at 3.393 ppm, and a signal at 3.532 ppm attributes to the alcoholic OH group *[20]*.

The ^{1}H NMR of BHETT in Figure-8 shows that similar signal peaks positions of aliphatic groups CH_2 and alcoholic group OH of thioglycol, but differences are signal of the proton adjacent to aromatic rings which appears at 8.017 ppm, disappearing triplet signal of thiol group at 1.936 ppm, and eventually, aliphatic group CH_2 that neighboring thiol group appears as triplet signal in BHETT instead of quartet signal in thioglycol. That means, the decomposition of PET was formed thioester groups by nucleophilic attack of thiol groups to carbonyl of ester groups and this analysis is compatible to results of IR analysis. The oligomer has more aliphatic groups CH_2 and aromatic single proton, and for this reason, peaks appear too height comparing with alcoholic groups OH (Figure-9).

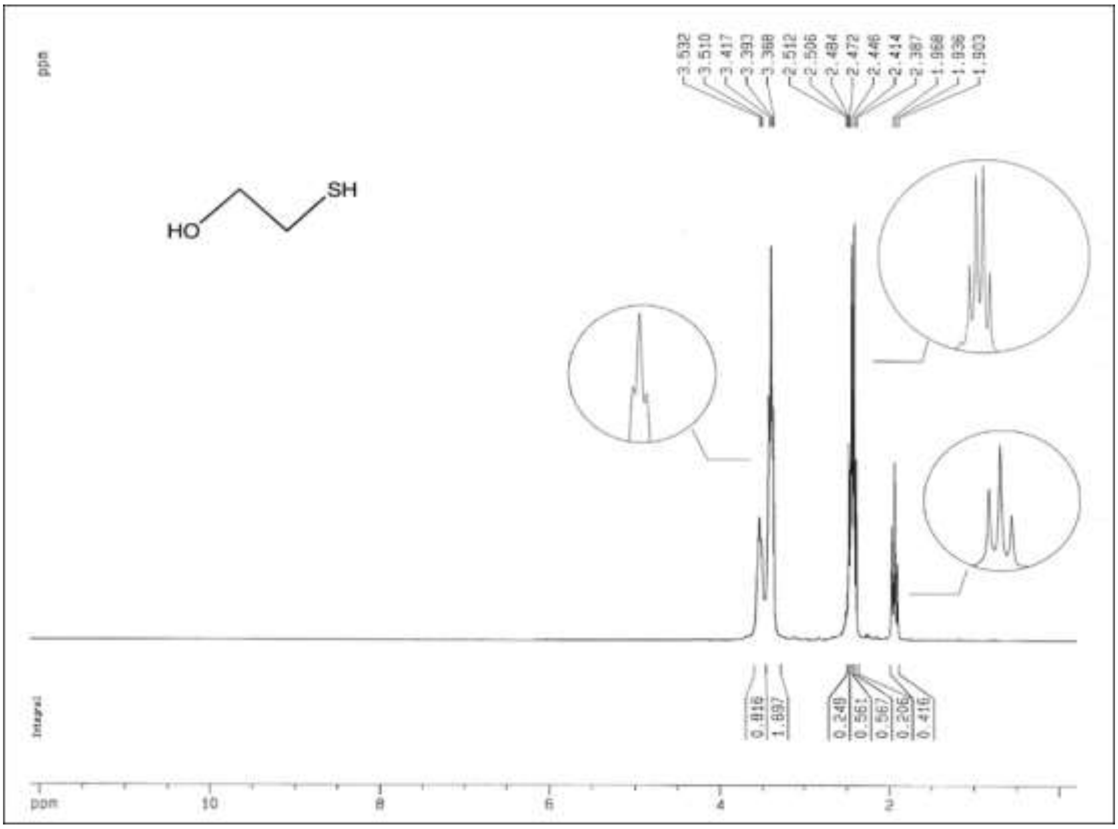


Figure-7: ^{1}H NMR spectra of thioglycol.

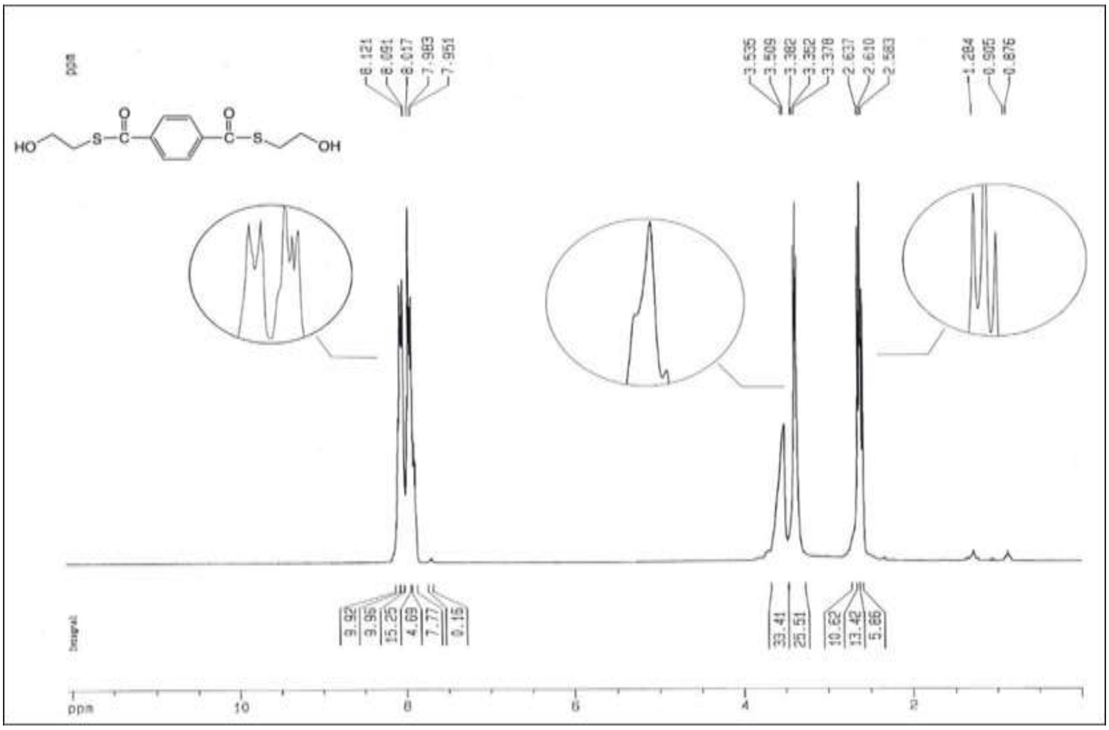


Figure-8: ^{1}H NMR spectra of BHETT (PET to thioglycol mole ratio is 1:6).

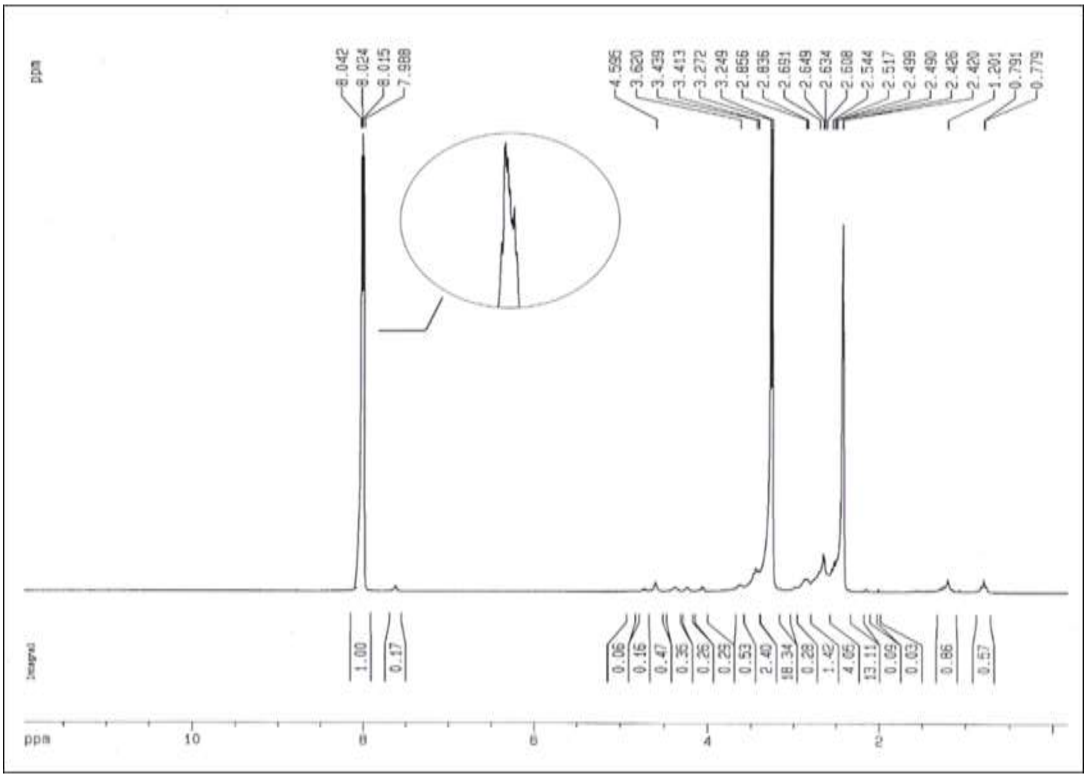


Figure-9: ^{1}H NMR spectra of oligomer of thiolyzed products (PET to thioglycol mole ratio is 1:6).

- CHNS analysis

The weight of elements (C, H and S) for BHETT monomer was analyzed and the results are in good agreement with these required by the proposed formula: $C_{12}H_{14}O_4S_2$, calculate: C 50.344%, H 4.943%, S 22.354%, found: C 51.024%, H 5.106%, S 22.975%.

It was found that compatibility of instrumental values with theoretical values. That means CHNS analysis is predicating characterization of other analysis (FTIR and NMR).

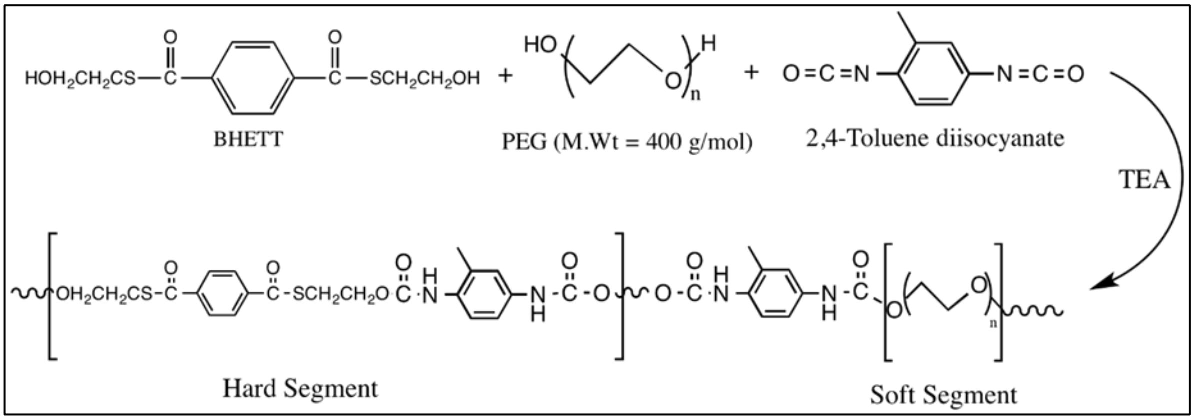
C. *Compression strength assessments*

Compression of polymer foam is one of the most important for the engineering applications. Generally, there are three important factors that affect at the softness and toughness polyurethane behavior; raw materials, percentage of reactant complements and foam density *[21]*. In this work, adding drops of water to mixture determine foam densities of prepared specimens, therefore 2-1 water drops is required to achieve 70-60 g/dm foam density.

The compression curves, as shown in Figure-10, gave three main observed regions: linear elasticity, flat plateau, and densification of material that causing sharp stress raise. There is an initial sharp increasing of stress curves at the first region, strain less than 6%, because of cell walls of the foam are restricted and starts to bend. This bending is completely returned back to initial dimensions when strain action is removed. Then, cell walls gradually buckle and slightly collapse with strain increasing, and that will reflect on wide area of compression chart. The sharp raising of curve at the third region happens when walls cell crashes together, this will compact wall cells and may return to initial dimensions after long period depends on foam elasticity *[22, 23]*.

According to these results, it can be confirmed that there is a strong dependence of stress–strain relations upon components proportion. Increasing of BHETT ratio percentage in polymer foams give more tough properties. That means thiolyised product takes a behavior as a hard segment in polymer chains, while PEG is a soft segment. Both hard and soft segments are illustrated in scheme-2 .

From Figure-10, it was observed that S1 is more elastic that gives less foam stress at linear elasticity region, while others curves are braked down after sharp increasing to form broad or sharp peaks at the same area due to collapse of BHETT hard segments. In addition, increasing of BHETT weight proportion gives high stress at lower strain values. Rigid foams and high stress at linear elasticity region have obtained by higher weighs proportion of BHETT in diol mixture, about 1.19 Mpa and 1.26 Mpa for 90% and 100% BHETT respectively.



Scheme-2: Illustrating of hard and soft segments of polyurethane.

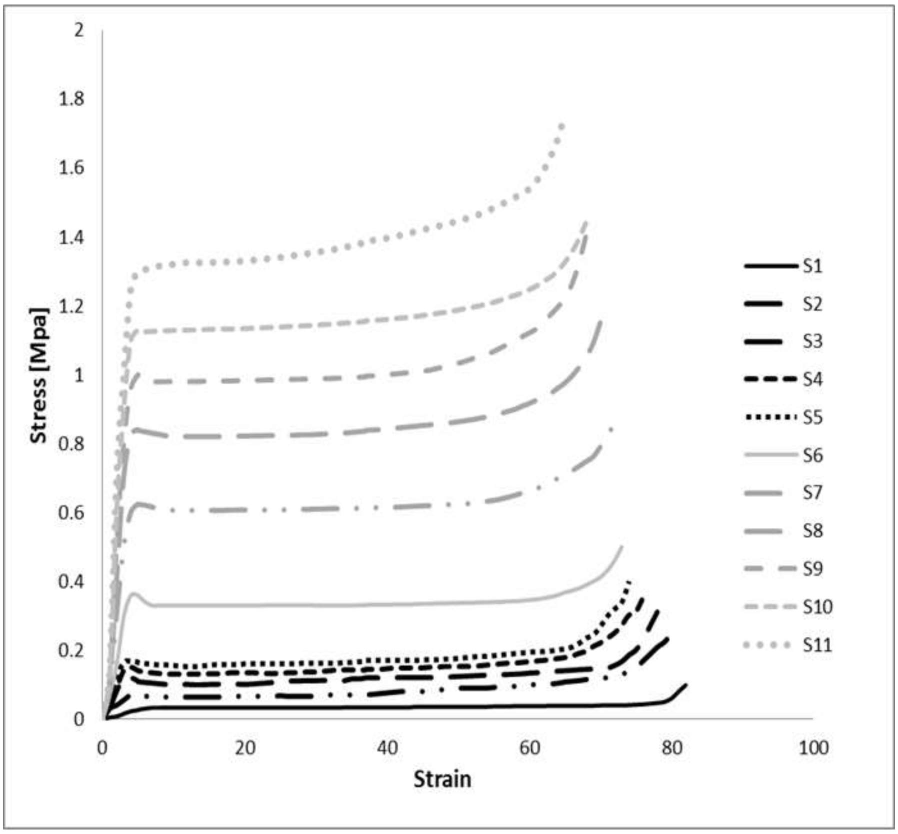


Figure-10: Compression curves of prepared specimens.

Conclusion

In summary, novel monomer from PET waste have successfully synthesized, characterized and determined thiolysis conditions. It has also observed by the results that 16 hour reaction time and 1:6 PET to thioglycol molar ratio were given the best yield of monomer, reaching to (40%). The characterization of new monomer by FTIR, ^{1}H NMR and CHNS analysis were improved nucleophilic attack of the thiol groups to the ester linkages along the PET backbone and obtained new thioester monomer (BHETT). On the other side, the new urethane polymers from BHETT with density 70-60 g/dm were prepared and found that

BHETT monomers behave as hard segments in polyurethane chains and give rigidity to PEG-TDI foam, which can be widely used in other various engineering applications.

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