Microwave Assisted Glycolysis of Poly(ethylene terepthalate) for Preparation of Polyester Polyols

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ABSTRACT: The generic aim of the present work is to reduce the time required for glycolytic depolymerization of PET by employing microwave irradiation instead of the conventional heating process. Glycolysis of PET was performed in the presence of glycols of different molecular weight under microwave irradiation. Experimental conditions like PET : glycol ratio, reaction time and concentration of glycerol were optimized to maximize the product yield. In the presence of ethylene glycol, bis-(hydroxyethyl) terephthalate (BHET) could be obtained in excellent yields in significantly lesser time (30 min) as compared to 8–9 h by conventional heating process. The BHET yield could further be increased by a second step glycolysis of the residual oligomers. This increased efficiency of the microwave assisted process has been attributed to the high microwave absorption capacity of glycols which results from their high loss factor. PET could also be glycolysed in the presence of higher glycols, however the reactivity of diols was found to decrease with increase in the molecular weight. The polyols obtained were reacted with aromatic diphenylmethane diisocyanate to prepare polyurethane foams, which were characterized by various techniques for determination of their physical, mechanical and structural properties. The compressive strength of the polyurethane foams was found to be inversely proportional to the molecular weight of the glycolysed polyol used for its preparation. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2779–2788, 2013

INTRODUCTION

Plastic wastes have been accumulating in the environment over the last several decades, resulting in a major "visual litter" problem.[1] To conserve the ecological balance, the practice of recycling plastic wastes is receiving more and more attention lately. PET is reportedly the most recyclable commodity plastic, however only a small fraction of this polymer is practically recycled, because of the relatively high cost of the recycled product.[2] The root cause, which renders the recycling process impractical, appears to be its inefficiency, particularly in terms of the energy requirements.

Tertiary recycling, more commonly known as feedstock recycling, refers to the process of converting plastic wastes into fuels or basic chemicals.[3] PET scrap can be chemically recycled by several processes including glycolysis, aminolysis, hydrolysis, acidolysis, alkalolysis, and alcoholysis, out of which only the former two have reached the level of commercial maturity.[3,4] The hydroxyl terminated oligomers prepared by glycolysis have been used as a raw material for preparing polymers like unsaturated polyesters,[5,6] UV curable films,[6] and polyurethanes.[7,8]

Glycolysis is an energy intensive process which requires high temperature and extended time periods thereby leading to the high cost of the final product. Technological innovations which can reduce the time required for glycolytic depolymerization are the need of the hour. In this context, the use of microwave irradiation as an alternate energy source has received much attention lately.[9] Microwave heating has several advantages over the conventional heating process, most important being the rapid heating rate that leads to reduced reaction time. Recent kinetic investigations on microwave aided glycolytic process have revealed that the apparent activation energy is substantially lower compared to the same process using conventional heating.[10]

Microwave assisted depolymerization of PET has been attempted in the presence of propylene glycol,[11] benzyl alcohol,[12] hydrazine,[13] ammonia,[14] alkali hydroxide,[15,16] ethylene glycol (EG),[9] and ethanolamine[9,17] to obtain industrially important chemicals.[12] However, in view of the large energy requirement for glycolysis with higher molecular weight glycols, most of the studies reported in the literature are restricted to

glycolysis with EG and Diethylene glycol (DEG). As, ~90% of the polyols, currently used for the production of polyurethanes are polyether based, which at present, are being derived from ethylene and propylene oxides,[18] we considered it of interest to reduce the energy requirements for preparation of polyester-ether based polyols, by using microwaves instead of the conventional heating process.

This article describes the use of microwave for preparation of polyester polyols from PET by reacting with diols of different molecular weight. The effect of introduction of a functional additive, glycerol on hydroxyl number (HN) of polyol has also been investigated. The resulting polyols were used to prepare polyurethane foams by reacting with isocyanate in the presence of surfactant, blowing agent and catalyst, which were further characterized by various techniques.

EXPERIMENTAL

Materials

Disposed off PET bottles were collected, washed, dried and used after removal of the polyethylene caps and the polypropylene label. The bottles were cut into small pieces (6×6 mm²) and the glycolysis experiments were performed in the presence of difunctional and trifunctional alcohols of varying molecular weight (EG, 2,2′-oxydiethanol (DEG, M.wt. 106), glycerol, polyethylene glycol 200 (PEG 200), polyethylene glycol 600 (PEG 600), polyethylene glycol 1000 (PEG 1000), and polyethylene glycol 1500 (PEG 1500), Merck. Zinc acetate dihydrate [Zn (CH₃COO)₂. 2H₂O, Merck] with a purity of 99% was employed as the trans-esterification catalyst. Diphenylmethane 4,4′-diisocyanate, a mixture of di- and triisocyanates (MDI) (Merck) and dibutyl tin dilaurate (DBTL) (Merck) were used without any further purification. Double distilled water was used throughout the course of this work.

Microwave Assisted Glycolysis

A domestic microwave oven (LG) with a magnetron source for microwave generation (2.45 GHz, maximum power: 900 W) was used for the purpose of glycolysis. PET pieces (10 g) together with requisite amount of glycol and zinc acetate (0.5%, w/w, PET) were introduced into a loosely stoppered reaction flask which was placed in the microwave reactor. Glycolysis experiments were performed at different molar ratio of PET : glycol: 1 : 2, 1 : 4, 1 : 6; both in the presence as well as absence of catalyst. The reaction was allowed to proceed at 450 W for extended time periods (30 min). After predetermined periods, the reaction mixture was filtered through a copper wire mesh (0.5 $\times$ 0.5 mm² pore size), and the remaining unreacted PET flakes were weighed to quantify the extent of PET conversion, as the ratio of mass of PET reacted to the initial mass of the flakes taken for the reaction. Tri-functional polyols were prepared by introducing glycerol in the reaction medium (3–30%, w/w) in addition to the diol. Transesterification of PET in the presence of higher glycols including DEG, led to the formation of a viscous liquid, which did not solidify on cooling. However, when the reaction was performed in the presence of EG, the viscous liquid solidified, to which was added excess of boiling water, for extraction of the catalyst (zinc acetate), bis-(hydroxyethyl) terephthalate (BHET) and other water soluble oligomers.

The resulting suspension was filtered and white crystals of BHET were obtained by repeated crystallization of the extract. The BHET yield was calculated as follows:

$$\text{BHET Yield } (\%) = \frac{\frac{m_{BHET}}{\text{M.Mass}_{BHET}}}{\frac{m_{PET}}{\text{M.Mass}_{PET}}} \times 100 \qquad (1)$$

where, m_{BHET} and m_{PET} refer to the mass of BHET and PET; M.Mass$_{BHET}$, M.Mass$_{PET}$ refer to the molecular mass of BHET (254) and PET repeating unit (192) respectively.

For comparison purposes, glycolysis was also performed at 180–190°C in an oil bath, under inert atmosphere in a four-necked round bottom flask, connected to a reflux condenser, N₂ gas inlet, thermometer and stirrer, the concentration of reactants being same. The results in terms of PET conversion and BHET yield were compared with those obtained under microwave irradiation.

Characterization Techniques

Thermal behavior of samples were investigated using Perkin Elmer Diamond STG-DTA-DSC in air and N₂ atmosphere (flow rate = 20 mL/min) in the temperature range of 50–800°C. A heating rate of 10°C/min and sample mass of 5.0 ± 0.5 mg was used for each experiment. Thin layer chromatography (TLC) analysis of glycolysate and BHET was carried out using chloroform : ethanol:: 90 : 10 eluent, as per the procedure reported previously.[9] The HN was determined using acetic anhydride, as per test method A, described in ASTM D 4274-99. Before determination of the HN, CHCl₃ was added to the liquid reaction mixture after removal of solid PET flakes. Subsequently, distilled water was added, which led to the formation of two distinct layers. The organic layer containing the glycolysed product was separated and subjected to vacuum distillation on a rotary evaporator to remove excess chloroform. An elemental analyzer (Elementar, Vario EL) was used to quantify the percentage of carbon, hydrogen and oxygen present in BHET and PET. Fourier transform infrared (FTIR) spectra of samples were recorded in the wavelength range 4000–600 cm⁻¹ using FTIR spectroscopy on a Thermo Fisher FTIR (NICOLET 8700) with an attenuated total reflectance (ATR) crystal accessory.

The viscosity-average molecular weight of PET was determined by solution viscometry. Samples were dissolved in a mixture of phenol and 1,1,2,2-tetrachloroethane (60/40, w/w) under heating, and the intrinsic viscosity [η] was measured using Ubbelohde suspension level viscometer at 25°C. The viscosity average molecular weight of PET was calculated using the following equation.[19]

$$[\eta] = 75.5 \times 10^{-3} \text{ mL/g } M_v^{0.685}$$

The intrinsic viscosity of the glycolysed polyols after extraction with chloroform was determined in methanol at 25°C. Waters (1525) gel permeation chromatograph (Milford, MA) equipped with styragel (HR-3 and HR-4, 7.8 $\times$ 300 mm²) columns along with Evaporating Light Scattering Detector (ELSD-2420) was used to determine the molecular weight and molecular weight

distribution of the polyols obtained post-glycolysis. Narrow molar mass polystyrene standards were used for calibration purposes.

The surface morphology of samples was studied using a Scanning Electron Microscope (Zeiss EVO MA15) under an acceleration voltage of 20 kV. Samples were mounted on metal stubs and sputter-coated with gold and palladium (10 nm) using a sputter coater (Quorum-SC7620) operating at 10–12 mA for 60 s. The average cell dimensions and standard deviations were determined by measuring the diameters of about 20 cells using inbuilt image processing software.

The density of the PU foam was determined by averaging the mass/volume measurement results of five specimens per sample following ASTM D1622-98 standard. The average value along with the standard deviation has been reported in the article. The compressive mechanical properties of the foams were determined using an Instron Universal Testing Machine (Model 3369) according to the ASTM D1621-00 standard. The samples (60-mm diameter and 36-mm length) were prepared in cylindrical Teflon molds. The cross-head speed was maintained at 3.54 mm/min. Compressive load was applied till the foam was compressed to approximately 15% of its original thickness and the compressive strengths were calculated based on the "10% deformation" method as per the standard procedure. At least three identical specimens were tested for each composition and the average results along with the standard deviation values have been reported.

Preparation of Polyurethane Foams

Polyurethane foams were prepared from tri-functional polyester polyols obtained by the reaction of PET with PEG of different molecular weights in the presence of 3% glycerol. Weighed amount of the polyester polyol, silicone oil surfactant (2%, w/w polyol), DBTL catalyst (1%, w/w polyol), and foaming agent (water) were mixed in a flat-bottom Teflon beaker and stirred mechanically for 1 min at 1000 rpm. Subsequently, requisite amount of MDI, as calculated according to the following formula was added and stirred vigorously for 30 s, after which the viscous liquid was poured into square box moulds (2 ×2 × 2 cm^3) and allowed to foam within.

$$m_{iso} \cdot n_{eq,iso} = [m_{H_2O} \cdot n_{eq,H_2O} + m_{poly} \cdot n_{eq,poly}] i_{NCO} \qquad (2)$$

where m_{iso}, m_{H_2O}, and m_{poly} refer to the mass of polyisocyanate, water and polyol respectively and $n_{eq,iso}$, n_{eq,H_2O}, and $n_{eq,poly}$ are the equivalent number of polyisocyanate (7.43 mmol/g), water (111.1 mmol/g) and polyol (estimated from the HN) and i_{NCO} is the desired NCO index (1.05) maintained for the formulation.[20] The polyols and foams were designated as PL and FM followed by a numerical suffix indicating the molecular weight of glycol from which it is derived. For example, the polyol derived from glycolysis of PET with PEG 200, will be referred to as PL 200 and the foam derived from PL 200 will be referred to as FM 200 respectively in the subsequent text. The foams derived from polyols obtained by esterification the presence of glycerol were designated as FMxGy, where x refer to the molecular weight of glycol and y refer to the percentage of glycerol present during glycolysis.

RESULTS AND DISCUSSION

Reaction with EG : BHET Formation

Microwave assisted glycolysis takes place at a substantially higher rate as compared to the conventional electrical heating process.[10] Reaction of PET with EG led to the formation of BHET and other oligomers of higher molecular weight. Higher oligomers, being water insoluble could be separated by addition of hot water followed by filtration.[7] The filtrate containing unreacted EG, BHET and other water soluble oligomers, was cooled to precipitate the BHET, which was subsequently purified by recrystallization.

The effect of reaction time and PET : EG ratio on the BHET yield has been reported in Figure 1. It can be seen that the BHET yield increases with the progress of reaction and interestingly, when the reaction was allowed to proceed for longer durations, the yield of BHET decreased, which can be attributed to the polycondenzation of BHET, predominating at the latter stages of reaction. From the reaction stoichiometry, a ratio of
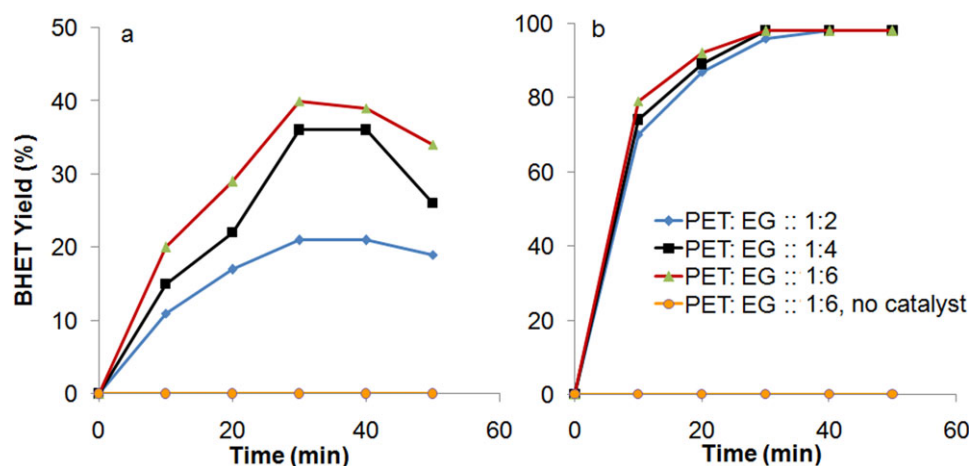

Figure 1. Effect of glycolysis time and PET: EG ratio on BHET yield (a) first step and (b) second step. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1 : 2 (PET : EG) appears to be sufficient for the reaction. However, the BHET yield reaches only ~20% after 30 min under these conditions (PET : EG ratio of 1 : 2). With increase in PET : EG ratio, the yield of BHET increases as can be seen from Figure 1. In comparison, the glycolytic process, when performed under electrical heating requires much longer time periods. Under electrical heating, the PET conversion reaches 100% after 8 h at 190°C, with a BHET yield of ~44% (PET : EG::1 : 6).

To further increase the BHET yield, it was decided to glycolyze the oligomers obtained as the residue in the first glycolytic cycle in another step, instead of performing the reaction for extended periods. For this purpose, pre-weighed oligomer's (first cycle residue) were reacted with EG and the yield of BHET was determined. It was observed that the entire amount of oligomer was converted to BHET within 10 min of microwave irradiation. In the absence of catalyst, no perceptible reaction between the glycol and PET could be observed. For the sake of brevity, the BHET yield obtained by performing noncatalyzed glycolysis under PET : EG ratio of 1 : 6 has been reported in Figure 1.

The DSC and TGA traces of neat PET, oligomers (first cycle residue) and BHET are presented in Figures 2 and 3, respectively. Neat PET exhibits a sharp melting point at 250°C. Glycolysis of PET result in depolymerization of the polymer leading to the formation of lower molecular weight oligomers, exhibiting a broad melting endotherm peaking at ~160°C. The carbon, hydrogen and oxygen content of PET flakes and recrystallized BHET, as determined by elemental analysis were found to compare well with the values predicted on the basis of their molecular formula. TLC was performed on the glycolysed products, and the TLC plate indicated three distinct spots, the lower one corresponding to BHET and the upper ones corresponding to higher linear oligomers.[21] The TLC plate of purified BHET obtained by repeated crystallization of its aqueous solution, exhibited a single spot, which further confirms its purity. This is further ratified by the presence of a sharp single endothermic
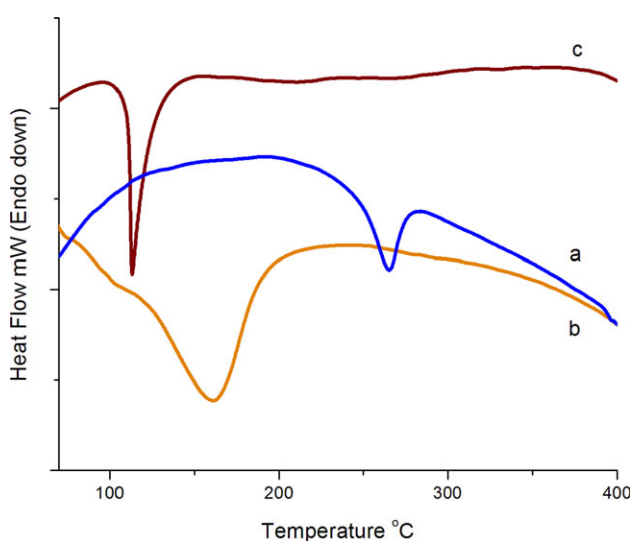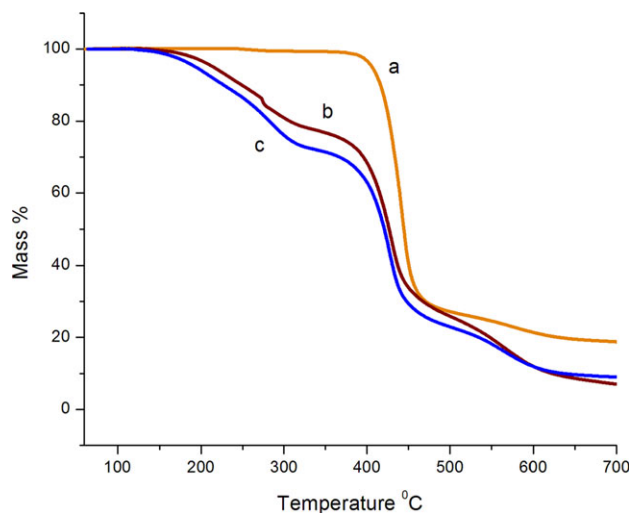

Figure 3. TG traces (a) PET, (b) Oligomers, and (c) BHET. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

peak at 110°C, observed in the DSC trace of recrystallized BHET.[22]

Glycolysis in the Presence of Higher Glycols

Effect of Reaction Time. The reaction of PET with higher glycols leads to the formation of a liquid oligomers, which could be separated from the water soluble reactants, that is, DEG/PEG and catalyst by water extraction. The reaction was followed by monitoring the extent of PET conversion, the variation of which has been plotted as a function of irradiation time in Figure 4. It is interesting to note that the effect of PET : glycol ratio on the extent of PET conversion is quite pronounced for lower glycols, like EG and DEG but seems to be insignificant for higher glycols, and hence for the sake of brevity, only the results obtained by the experiments performed using PET : Glycol :: 1 : 2 are being presented here. It can be seen that the maximum level of PET conversion could be achieved within 30 min of irradiation, while under the same PET : glycol concentrations; the reaction takes ~9 h to reach the same level of
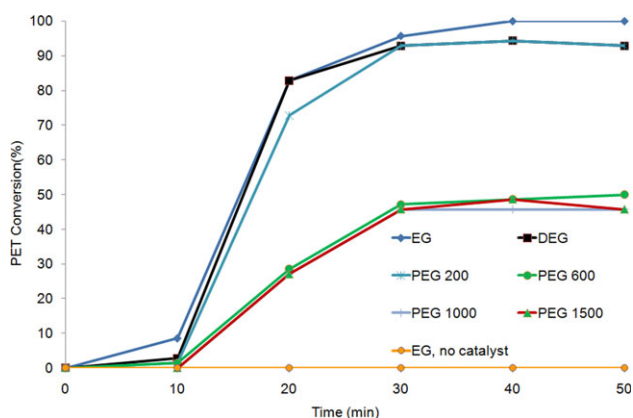

Figure 2. DSC traces (a) PET, (b) Oligomers, and (c) BHET. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4. Effect of glycolysis time and molecular weight of glycol on the extent of PET conversion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

depolymerization. Our studies also indicate that glycolytic depolymerization does not take place in the absence of catalyst even if the reaction is allowed to continue for extended time periods at higher PET : glycol ratio. Unreacted PET could not be detected in the reaction medium after ~30 min of reaction with EG/DEG, but with higher glycols, the extent of PET conversion was much lower (~48%, PET : PEG 1000 :: 1 : 6), which indicate that the reactivity of glycols decrease with increasing molecular weight of glycol.

The viscosity-average molecular weight of PET was determined by solution viscometry, which revealed that the M_v of the PET films decreased from an initial value of 27,431 to 1521 ± 130 after glycolysis for 30 min in the presence of glycols of lower molecular weight (DEG and PEG 200). The M_v of the remnant PET was slightly higher, when glycols of higher molecular weight were employed ($M_v = 3221$ for PET glycolysed with PEG 1500). The glycolytic process proceeds with the diffusion of the glycol to the surface of PET. The penetration of the solid polymeric matrix with the glycol results in the swelling of the polymer and the reaction finally results in the depolymerization of PET into polyesters of lower molecular weight. The surface of the PET films after glycolysis with different glycols was studied by SEM imaging, the results of which are illustrated in Figure 5. It can be seen that the surface of neat PET [Figure 5(a)] is smooth, however, post-glycolysis the surface becomes corrugated as a result of the penetration by the glycols and removal of the transesterified products formed as a result of the reaction.

Physical Properties of Polyols. One of the most important characteristics of any polyol is its HN (mg KOH/g), and the preparation of rigid PU foam requires polyols with a much higher HN and viscosity than the polyols for flexible polyurethanes.[23] The HN of the glycolysed products obtained after the reaction of PET with increasing molecular weight glycols after microwave irradiation for 30 min is listed in Table I. The intrinsic viscosities along with the M_n, M_w, and M_z values, as obtained by GPC are also presented in table. There was not much variation in the HN after ~30 min of reaction. It is to be noted that prior to determination of the HN, the liquid sample was extracted with chloroform, to eliminate the contribution of water soluble reactants, that is, DEG/PEG and side products, that is, EG, to the HN. Our studies reveal that microwave assisted glycolysis led to formation of polyols which are suitable to be used for PU preparation, both rigid as well as flexible, depending on the glycol used for its preparation. The functionality of the glycolysed product could be increased by introduction of a trifunctional additive (glycerol) to the reaction mixture, which led to an increase in the molecular weight of the
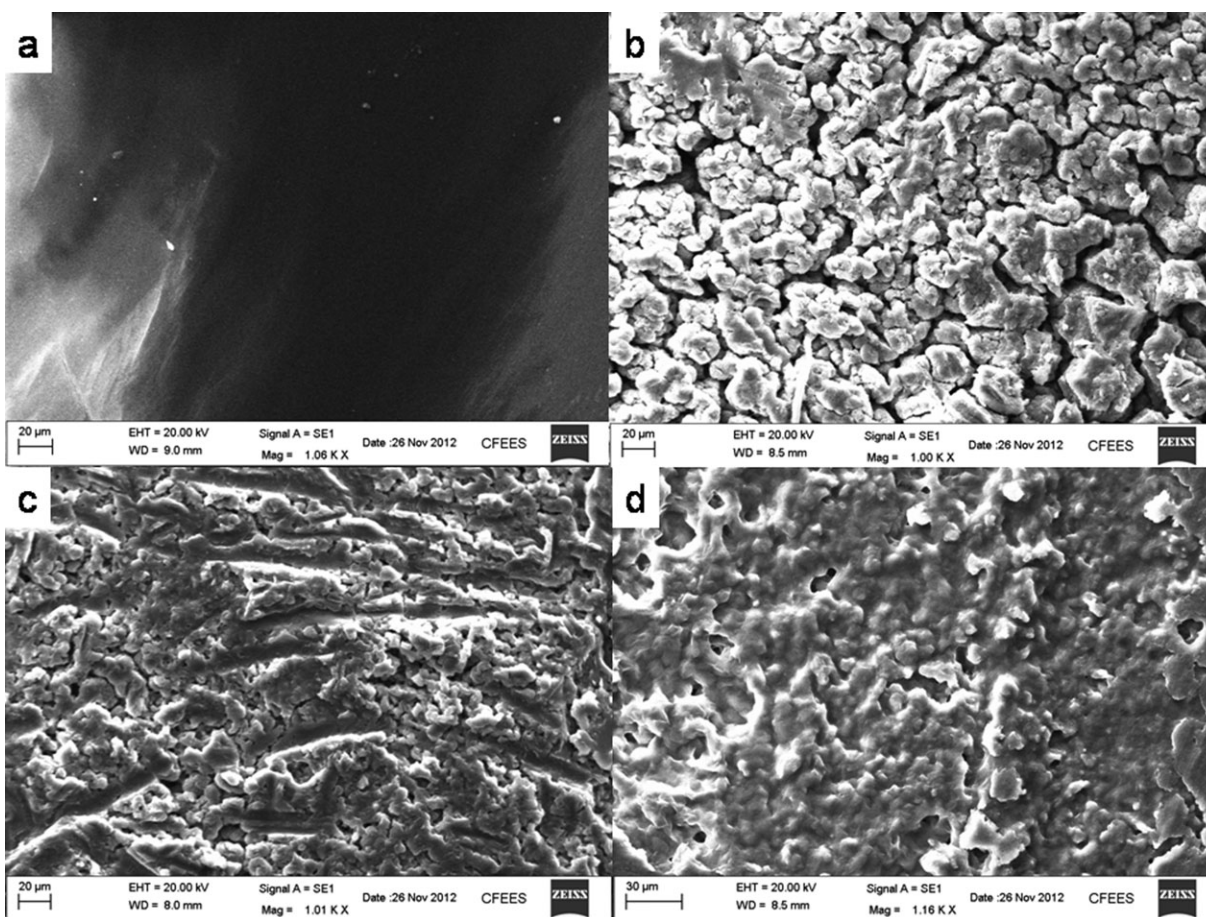

Figure 5. Scanning electron micrographs of (a) PET films and residual PET after reacting with (b) DEG (c) PEG 600 (d) PEG 1500.

Table I. Characteristics of the Glycolysed Polyols

Polyol	HN (mg KOH/g)	[η] (dL/g)	M_n	M_w	M_z	PDI
PL 106	410 ± 15	0.019	330	456	564	1.7
PL 200	250 ± 10	0.029	558	995	1529	1.8
PL 600	110.3 ± 5	0.045	1114	2025	3074	1.8
PL 1000	86.4 ± 4	0.051	1745	3078	4436	1.7
PL 1500	32 ± 3	0.056	2776	4080	5508	1.5

glycolysed product. The glycolysed product has a lower HN in this case, and the decrease in the HN with increasing amount of glycerol is presented in Figure 6. It was observed that after 8% of glycerol addition, HN did not decrease further.

The intrinsic viscosity of the glycolysed polyols as determined in methanol at 25°C are also reported in Table I. As expected, with increase in the molecular mass of glycol employed for the transesterification of PET, the intrinsic viscosity of the resulting polyol also increased. The M_n, M_w, and M_z values, as obtained by GPC are also presented in table. A broad molecular weight distribution was observed in all cases, and the same can also be judged from the huge variation in the average molecular weights (Table I). From Figure 6, it can be seen that transesterification in the presence of glycerol leads to formation of polyol with increased viscosity. Interestingly, comparison of Table I and Figure 6 reveal that trifunctional polyols which are formed in the presence of glycerol, exhibit slightly lower viscosities than their linear analogues. This can be attributed to the branched nature of the trifunctional polyol, which result in a compact globular structure which are less entangled than the linear diols produced in the absence of glycerol.

Structural Characterization

The reaction of PET with glycols was also studied by FTIR analysis. The FTIR spectra of PET, PEG 200, a representative glycolysed PET oligoester (PL 200) and the foam obtained there from (FM 200) presented in Figure 7. The spectrum of Poly(ethylene glycol) exhibit characteristic absorption bands due to ether

stretching (C—O) at ~1050–1150 cm^{-1}, with maxima at 1150 cm^{-1}. Characteristic alkyl (R—CH$_2$—) stretching at ~2850–3000 cm^{-1} was also observed, along with hydroxyl group absorption ranging from ~3200–3600 cm^{-1}. In comparison, the glycolysed product exhibit absorption at 1715 cm^{-1} due to —C=O stretching, which can be attributed to the presence of ester group, formed as a result of glycolysis of PET. This peak is also present in the spectra of neat PET. The absorption band at ~3200–3600 cm^{-1} can be attributed to the presence of free hydroxyl groups present in glycolysed PET oligoesters. Strong peaks corresponding to the urethane linkages at 1650 and 1550 cm^{-1} (CO—NH, NH$_2$), O—C—O 1270 cm^{-1} and from C—O 1100 cm^{-1} [24] were observed in the spectrum of the PL 200. Furthermore, additional peaks at 1640 cm^{-1}, typical of allophanates, and at 1450 cm^{-1} corresponding to the isocyanurate group are also present which are a result of the secondary reactions of PU, for example, resulting from reactions between isocyanate and urethane groups.

Microwave Assisted Heating

The energy associated with the microwave frequency (2.45 GHz, 0.0016 eV) employed for the glycolytic depolymerization is too small to cleave covalent chemical bonds, which makes it apparent that these radiations cannot induce chemical reactions, and the enhanced efficiency observed with the microwave assisted glycolytic process can only be attributed to the efficient heating under the conditions employed during microwave irradiation.[25] This is commonly known as the "microwave dielectric heating" effect. The physical characteristic property of any material, which can be used to quantify its ability to convert
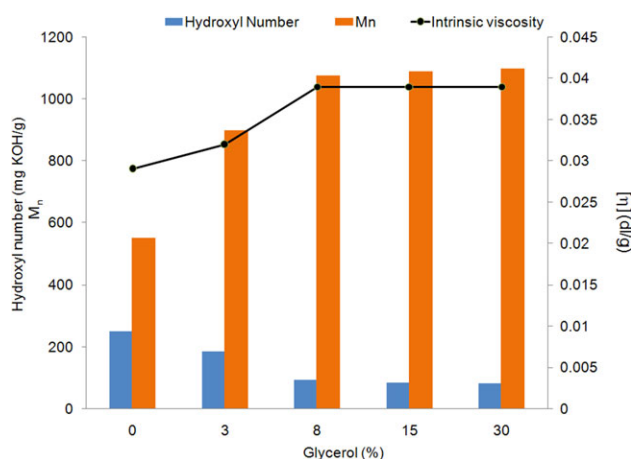
Figure 6. Effect of functional additive on HN, intrinsic viscosity and molecular weight of the glycolysate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
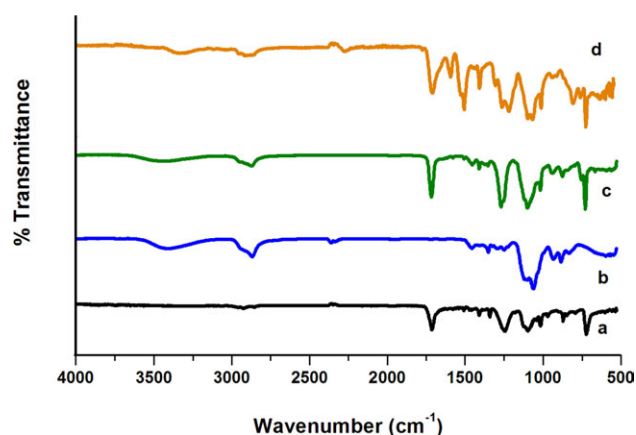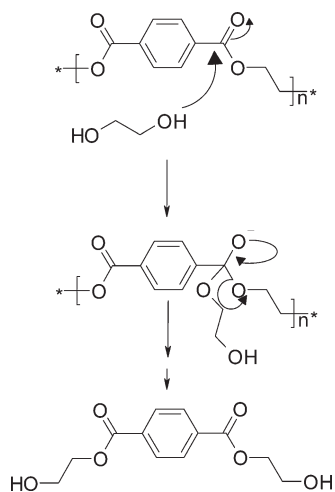
Figure 7. FTIR spectra of (a) PET, (b) PEG 200, (c) polyester polyol derived there from (PL 200), and (d) FM 200 G3.

Scheme 1. Reaction of PET with ethylene glycol to form BHET.

electromagnetic energy into heat, is its loss factor (tan δ), which in turn is defined as the ratio of dielectric loss to its dielectric constant. In the present study, the glycols, apart from serving their primary role as the transesterification agent, also play an extremely important function of an proficient microwave absorbing fluid, because of their high loss factors (tan δ_{EG} = 1.305).[26] Because of the presence of intramolecular hydrogen bonds in lower glycols, particularly EG and DEG, these exhibit higher dipole moments than their higher molecular weight homologues, which in turn leads to more rapid heating in these diols. This can also be used to explain the rapid PET conversion observed when the reaction is carried out in the presence of lower glycols. However, in the conventional process, the reaction mixture in contact with the vessel wall is heated first, which is then conducted through the medium. In this case, the potential of glycols as efficient microwave absorbers remains untapped, and this can be used to explain the difference between the observed rates of the two processes.

Mechanism of Esterification
A representative scheme of the reaction of PET with EG is presented in Scheme 1. The lone pair available on the oxygen atom of the EG attacks the carbonyl group in the polyester. The hydroxyl-ethyl group of EG then forms a bond with the carbonyl carbon of the polyester, breaking the long chain into short chain oligomers, which finally break down to BHET.

Glycolysis of PET has been reported to be a diffusion controlled process, and its rate depends on a number of parameters including reaction temperature, PET : EG ratio, and the type and amount of catalyst used.[27,28] Transesterification catalysts are routinely employed to increase the rate of PET glycolysis. Different transition metal based carboxylates have been investigated for their catalytic ability toward glycolytic depolymerization and Zn has been reported to be the most active.[6,29] The active transition metal forms a complex with the carbonyl functionality of PET, facilitating the attack of glycol on the polyester.[30] This leads to the glycolytic depolymerization of the parent polymeric chain into its oligomers.

Polyurethane Foam from Polyester Polyols
The process of polyurethane foam formation was monitored by measuring the duration of cream time, gel time, and tack-free time which are listed in Table II. This exothermic foaming process is initiated almost instantaneously upon mixing of the reagents and the reaction mixture continues to expand till the resulting foam solidifies as a result of progressive crosslinking. Cream time and gel time are critical in industrial formulations. For practical applications in injection technology, the cream time has to be more than the injection time and the foam should expand and fill the form in approximately the same time as the gel time. The cream time and gel time recommended by reactivity profiles of injection technology are 4–8 and 30–60 s, respectively.[8] It can be seen from the table that the foam rising (cream time) begins approximately within 15 s of mixing and solidifies completely (tack-free time) within 52–62 s. The density of the foams obtained from different polyols are also reported in Table II. It can be seen from the table that with increase in the molecular weight of the polyol used for preparation of foam, its density increases. This was also confirmed by surface morphological studies, and the images in this regard are presented in Figure 8. The average cell size of the foam along with the standard deviations was also determined and is reported in Table II. As can be seen from the figure, the foams possessed cells with uniform sizes.

Thermal Characterization of PU Foams. Figure 9(a,b) present the TG trace of polyurethane foams prepared by the reaction of methylene isocyanates with PET glycolysates under air and N_2 atmosphere, respectively. It can be seen that all the samples exhibited similar degradation behavior under similar conditions, irrespective of the molecular weight of glycolysate used for its preparation. Under air atmosphere, three-step decomposition

Table II. Characteristics of Polyurethane Foam Derived from Glycolysed PET

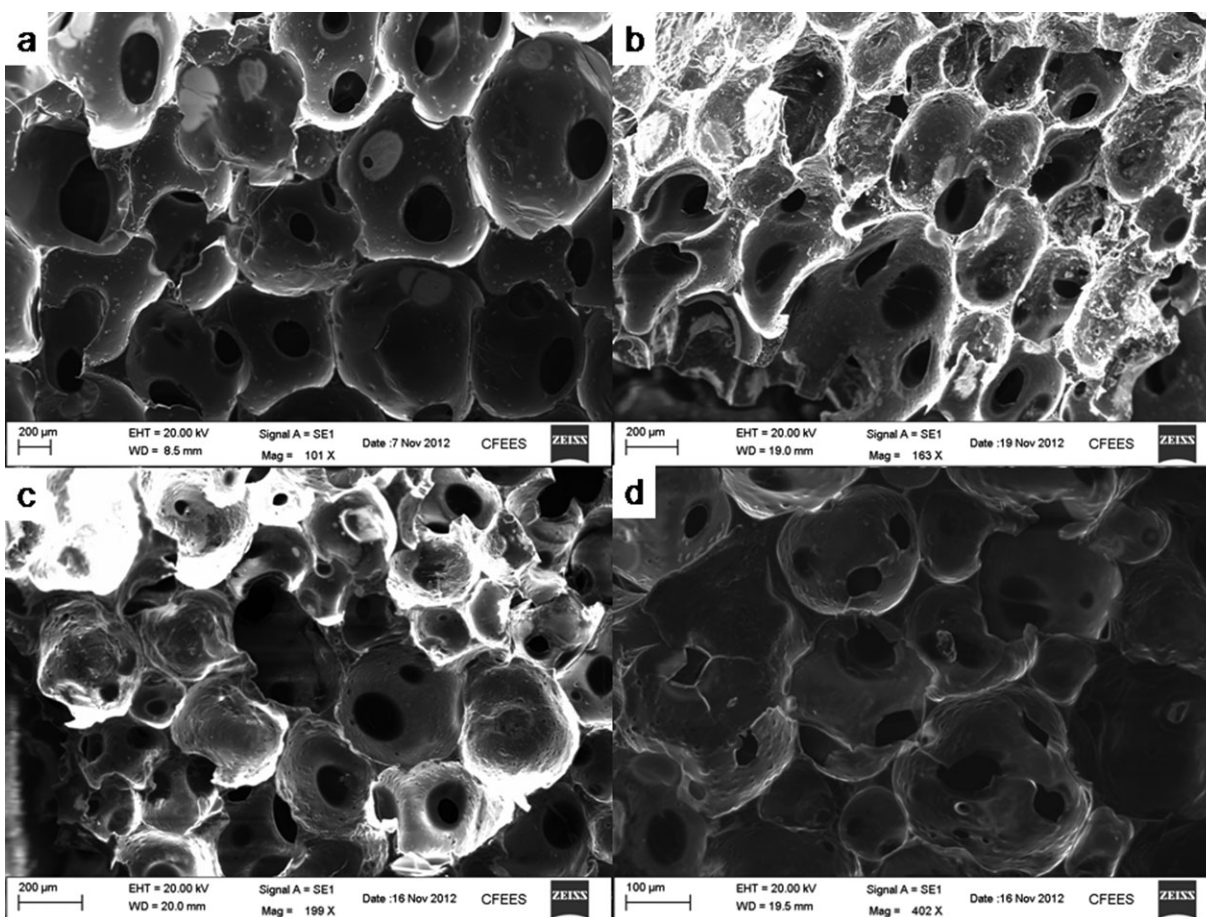| Foam designation	Cream time (s)	Gel time (s)	Tack free time (s)	Density (kg/m^3)	Cell size (μ)	Compressive strength (KPa)[a]	Young's Modulus (KPa)
FM 106 G3	14	31	52	82.1 ± 10.1	891 ± 72	232.4 ± 13.2	5560 ± 270
FM 200 G3	14	32	60	132.4 ± 9.7	797 ± 77	212.3 ± 12.1	3820 ± 190
FM 600 G3	15	36	62	167.1 ± 7.9	341 ± 93	11.9 ± 0.9	68 ± 3.4
FM 1000 G3	15	39	60	172.1 ± 7.7	316 ± 62	5.9 ± 0.4	64 ± 3.2
FM 1500 G3	15	38	61	185.3 ± 7.1	223 ± 43	5.1 ± 0.3	40 ± 2.1

[a]Values at 10% strain.

Figure 8. Scanning electron micrograph of representative polyurethane foams (a) FM200G3, (b) FM600G3, (c) FM1000G3, and (d) FM1500G3.

was observed in all samples. The minor mass loss at ~120–140°C can be attributed to the loss of the moisture/ water content of the foam. The second decomposition step at 270–280°C occurs due to the thermal degradation of the polymer, and the final mass loss step at 510°C results from the combustion of the

remnant. Our results are consistent with those reported previously, where a similar TG profile has been reported.[31–33] The TG profiles under N_2 atmosphere exhibit mass loss at two characteristic regions at 110 and 280°C. As expected; the char content was much higher under N_2 atmosphere as the mass loss
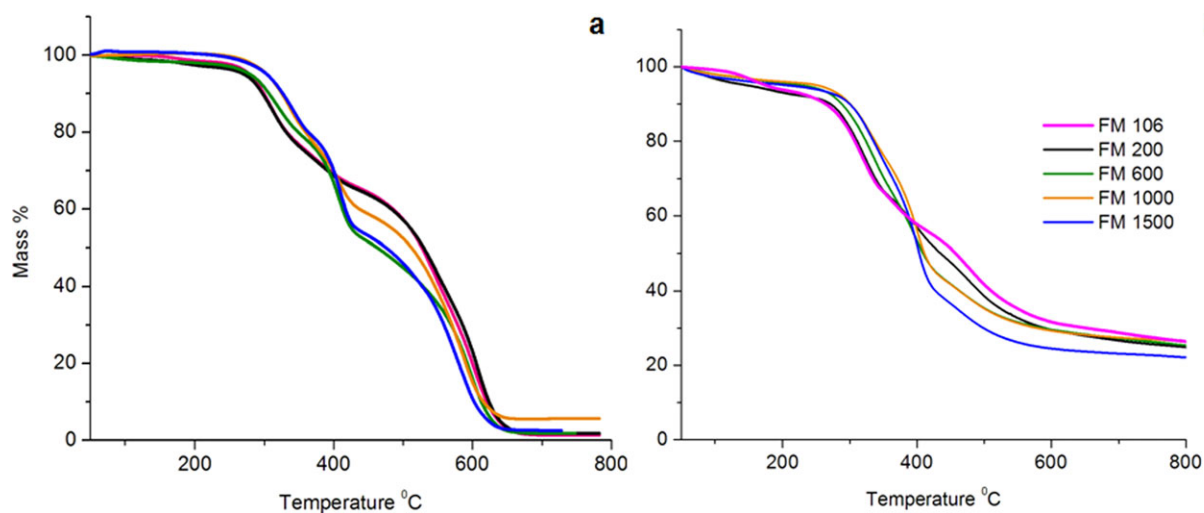

Figure 9. TG traces of polyurethane foams under (a) air and (b) Nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Results of Thermogravimetric Analysis

Foam designation	T_{onset1}	T_{max1}	T_{end}	Char yield at 600°C
FM 106G3	277.5	319.8	579.8	31.1
FM 200G3	293.7	320.1	598.1	29.6
FM 600G3	289.8	331.1	594.2	29.7
FM 1000G3	301.6	331.4	592.1	29.2
FM 1500G3	299.1	333.1	592.2	24.5

due to combustion of the pyrolyzed sample is absent. The characteristic temperatures in terms of T_{onset}, T_{max}, T_{end}, and char yield at 600°C (under N_2 atmosphere) are reported in Table III. The results indicate that all the foam samples could be safely used in service till a maximum of 270°C, without undergoing any major thermal degradation.

Mechanical Properties of Foams. The mechanical properties of the foams were evaluated under compression mode. Typical stress–strain curves are presented in Figure 10. The compressive strengths of the foams at 10% strain are reported in Table II. It can be seen from the figure that all the foam samples exhibit similar profile, that is, initial linear elasticity at low stresses, followed by an extended plateau. This feature is more pronounced in the foams prepared using lower glycols (Figure 10, inset). The observed initial linear elasticity region arises primarily from the bending of cell struts, and stretching of the membranes in the cell walls. The subsequent broad plateau is a result of the plastic collapse or cell wall buckling of the foam, which is more commonly referred to as the collapse stress.[34] It is this extended plateau, which endows the foams with their high compressibility and enables them to exert a relatively constant stress up to high strain levels. This plateau finally terminates in a regime of
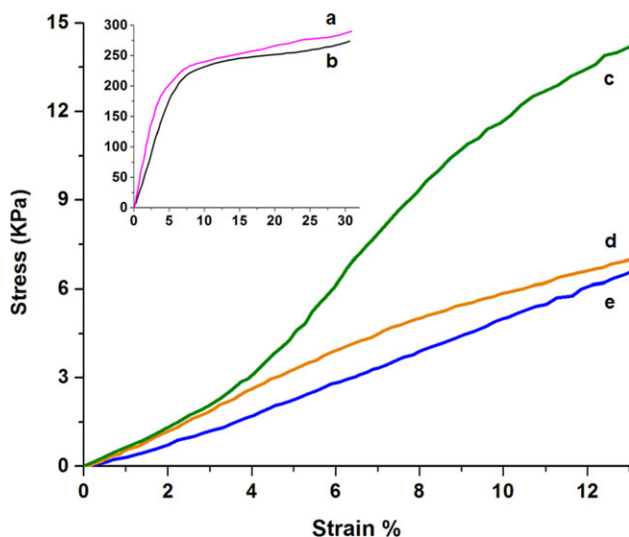

Figure 10. Compressive stress–strain relationship for foams in compression mode (a) FM106G3 (b) FM200G3, (c) FM600G3, (d) FM100G3, and (e) FM1500G3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

densification. The compressive strength of the foams was found to be inversely proportional to the molecular weight of the glycol used for its preparation. The initial linear region was used to determine the modulus of the foams, the results of which are reported in Table II. It can be seen that the foams prepared using glycols of lower molecular weight are rather rigid and the flexibility of the foams is directly proportional to the molecular weight of the glycolysate used for its preparation. It is the high molecular weight poly(ethylene glycol) unit which is responsible for imparting flexibility to the polyurethane foams.

CONCLUSION

Discarded PET bottles were catalytically glycolysed with diols of different molecular weight (62–1500) under microwave irradiation in the presence of zinc acetate (0.5%, w/w). The reaction time required for glycolysis could be significantly reduced (~30 min) by the use of microwave as compared to the conventional thermal glycolytic process, which requires a minimum of 8–9 h to reach the same level of depolymerization. The process could be successfully employed for preparation of BHET by performing the reaction in presence of EG. The effect of reaction parameters like PET : glycol ratio and reaction time were optimized to achieve maximum PET conversion and BHET yield. The studies revealed that performing a second step glycolysis was more successful in increasing the BHET yield, as compared to extended exposure to microwave, which in turn led to the reverse polycondensation reaction. PET could also be glycolysed in the presence of higher glycols, however the reactivity of diols was found to decrease with increasing molecular weight. Glycolysis in the presence of trifunctional additive, glycerol, led to the formation of functionalized polyols, which were used to prepare polyurethane foams. The physical, mechanical, and thermal properties of the polyurethane foams were determined and their cellular structures were investigated by scanning electron microscopy. The foams possessed cells of uniform dimensions, and the flexibility of the foam was found to be directly proportional to the molecular weight of the glycol used during PET glycolysis.

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