Straightforward Manufacturing of Polyurethane Adhesives and Foams from Post-consumer Poly(ethylene terephthalate) (PET) Bottles

EDINA RUSEN[1], ALEXANDRA MOCANU[1,2,*], DANA FIAT[3], ANCA MADALINA DUMITRESCU[4], PAUL OCTAVIAN STANESCU[1], AUREL DIACON[1]

[1]Politehnica University of Bucharest, Department of Bioresources and Polymer Science, 149 Calea Victoriei, 010072, Bucharest, Romania

[2]Beta Meg Invest Srl, 27A Prof. Dr. Mihail Georgescu Str., 024033, Bucharest, Romania

[3]ICECON S.A, Research Institute for Constrcution Equipment and Technology, 266 Pantelimon, 021652, Bucharest, Romania

[4] Politehnica Politehnica of Bucharest, Centre for Technology Transfer in Process Industries (CTTPI), 1 Gh. Polizu Str., Bldg A, Room A056, 011061, Bucharest, Romania

The aim of the current study was to obtain materials presenting a large scale of applications (polyurethane adhesives and foams) through a one-pot synthesis starting from post-consumer poly(ethylene terephthalate) (PET) bottles. The PET depolymerization was carried out using diethylene glycol (DEG) and catalyst (zinc acetate) in a microwave reactor. Using the obtained depolymerization mixture, different polyurethane adhesives or foams formulations were developed. The adhesives mechanical properties were tested affording samples with tensile shear resistance suitable for commercialization. The polyurethane foams testing confirmed the obtaining of rigid structure with good thermal insulation properties.

Keywords: PET, microwaves, adhesives, polyurethane foams, one-pot synthesis

Polyurethanes are used in the manufacture of flexible or rigid foams, surface coatings or sealants, adhesives, elastomeric products for high performance tires. The world consumption of polyurethanes in 2000 was about 8 million tons, with a global growth averaging around 3–4% a year [1]. Polyurethane products are represented by polymers formed through the reaction of a polyalcohol with a polyisocyanate, both containing on average two or more functional groups per molecule. The iscocyanate component is usually aromatic, most commonly used are 2,4 or 2,6- toluene diisocyanate (TDI) and 4,4'-methlylene diphenyl disocyanate (MDI). The polyol component can consist of an aliphatic glycol, 1,4-butan-diol, a polyether polyol or a polyester polyol with hydroxyl end-groups with relatively low molecular weight.

In an effort to promote environmental protection different alternatives have been developed for the polyol component utilizing either biomass components (soy oil and proteins, lignin, castor oil, cellulosic waste etc.) [2-7] or different types of plastic materials [8].

The chemical modification of different raw materials such as castor oil, soy extract, rape seed oil, the hydroxyl index of the polyol component can be controlled leading to the increase of the reactivity towards the isocyanate component [5]. Nevertheless, regardless of the provenience of the raw materials, this approach typically involves successive fabrication steps in the manufacturing of the polyol component, thus leading to a considerable cost increase of the end product [5-8].

The utilization of PET waste for the fabrication of polyurethane products permits the realization of innovative products with added value given a PET production of 49 million tons/year in 2011 [9, 10]. Over 1 million tons of PET waste are recycled every year in Europe, due to the environmental policy imposed by European Union [11]. While part of PET waste is converted into energy [12], most of the resulted derivatives from PET processing can be used as raw materials for certain applications as fibers [13], adhesives [8], synthetic dyes [14], polyurethane foams [15], concrete composites [16] leading to cost savings in the manufacturing type of products.

In our previous studies, we have presented PET glycolysis using different PET/DEG ratios and reaction conditions [17, 18]. The current study aims at obtaining materials for large scale applications (polyurethane adhesives and foams) through a one-pot synthesis starting from post-consumer recycled PET bottles.

The advantage of our approach consists in low production costs of the final products due to the straightforward manufacturing strategy and low energy consumption through the use of microwaves for a shorter reaction time. The final products are well suited for marketing presenting properties comparable with current assortments on the market. Another important advantage is the total lack of side products. The simplicity of our approach for the reutilization of PET waste is presented in scheme 1.

Experimental part

Materials and Methods

Polyethylene terephthalate (PET) (from post-consumer bottles) having a molecular weight Mn=25 000 g/mol was used as flakes. Diethylene glycol (DEG) (Fluka), zinc acetate (Fluka), methylenediphenyl diisocyanate (MDI) (Aldrich), neoprene GN (NW) (Aldrich) Mn= 100 000, toluene (Aldrich), PETOL PA - 500-5D (Oltchim S.A) (Hydroxyl number=490-530 mg KOH/g), castor oil (Aldrich) were used as received.

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* email: mocanu.alexandra53@yahoo.com

Depolymerization - glycolysis of PET

The reaction was carried out using a microwave reactor equipped with a mechanical stirrer, condenser, timer and thermostat, the experimental set-up is presented in figure 1. The experiments involved 150 g of PET, 75 g of DEG and 0.75 g of zinc acetate as catalyst (0.5% by weight of PET). The reaction was performed under nitrogen at a temperature of 220°C under continuous stirring for 2h.

Polyurethane adhesives

The first stage consisted in the premixing of the PET glycolysis product with the NW solution for a good homogenization (2 min stirring). To the obtained mixture, the MDI desired quantity was then added and stirring was realized for another 2 min prior to the brush application of the adhesive on the surface of the standardized test pieces.

Polyurethane foams

The component A was obtained by mixing the PET glycolysis product with PETOL PA -500-5D, castor oil and water. The component B consisting in MDI was added to component A and stirred for homogenization, creaming time - 1 min, followed by the rising step.

Characterizations

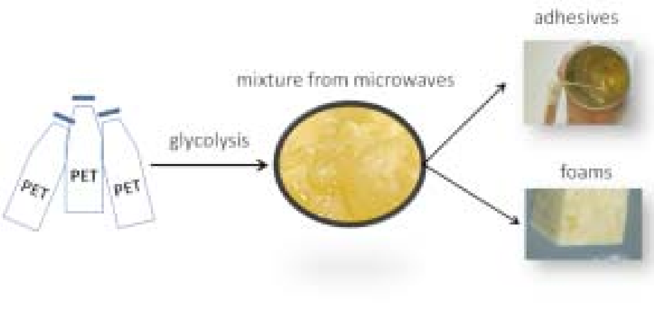
Molecular weights were determined by gel permeation chromatography (GPC) using a *PL-GPC 50 Integrated GPC/SEC System (Agilent Technologies)* apparatus equipped with a refractive index detector and THF as solvent.

The mechanical properties of adhesives were measured using an Instron 3382 equipped with 2 kN cell at room temperature (22±1°C) and 50±5% relative humidity. The material used for the test pieces derived from *Fagus sylvatica L.* (density 700 ± 50 kg/m^3, humidity content 12 ± 1 %) and the thickness of the bond was 0.1 mm. The tensile shear stress for lap joint adhesive testing was realized according to SR EN 205:2003 (Adhesives - Wood adhesives for non-structural applications - Determination of tensile shear strength of lap joints).

The mechanical properties of the polyurethane foams were measured using a Tinius Olsen equipped with a 10 kN cell. For the determination of the thermal conductivity of the insulation materials a Hesto Elektronik -CE/HLC A90 apparatus was used. For the determination of the water uptake by immersion a temperature controlled room (-20°C…60°C), a humidity sensor, a precision balance and a temperature controlled oven (5°C…250°C) were utilized.

Results and discussions

The first step in the realization of this study consisted in the obtaining of the PET derived polyol component through a glycolysis reaction using DEG (PET:DEG 2:1 weight ratio) under microwave irradiation (P=800 W). Based on our previous study [17], the selected reaction conditions were: temperature 220°C, reaction time 2 h and zinc acetate as catalyst. The PET glycolysis reaction and the experimental set-up are presented in figure 1.



Scheme 1. One-pot synthesis of polyurethane adhesives and foams

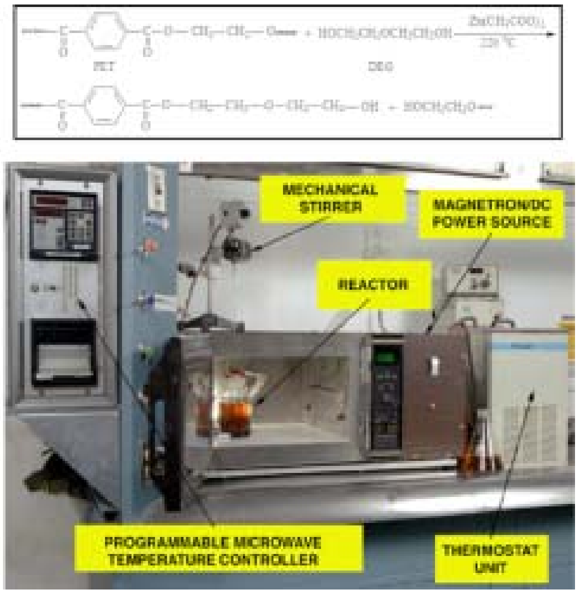


Fig. 1. PET glycolysis reaction and the experimental set-up

The GPC analysis of the glycolysis product, presented in figure 2 was realized in order to determine its molecular weight distribution and suitability for further applications. The results reveal the presence of three types of oligomers with molecular weights of 1503 g/mol, 507 g/mole and 209 g/mol in a ratio of 78.55%, 17.40% and 4.05% respectively. These values were determined from the respective peak areas presented in the chromatogram (highlighted results in fig. 2).

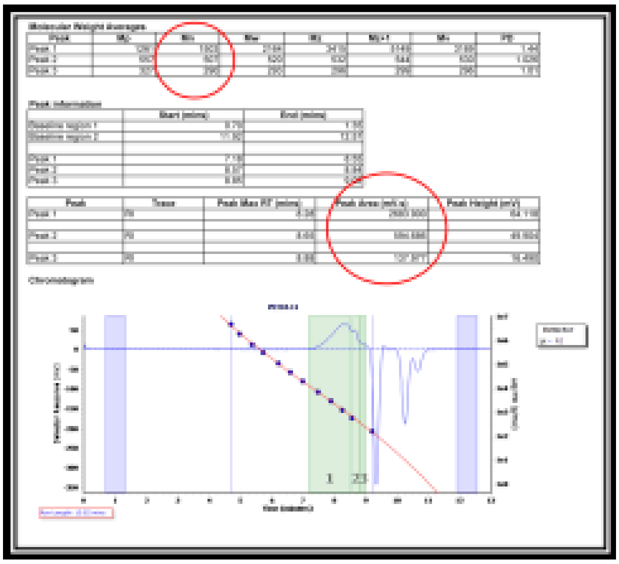


Fig. 2. GPC analysis of the PET glycolysis product

Microwave irradiation has proven an efficient heating source for chemical reactions [19]. It can improve reaction kinetics [20] or allow the attaining of higher conversion or selectivity[21]. Microwaves can permit a more uniform and selective heating [22] offering a more greener approach for the realization of chemical reactions[23]. The oligoesters obtained from the glycolysis of PET waste can be further reacted with aliphatic diacids in order to obtain polyol polyesters suitable as starting material for polyurethane adhesives [8]. However, the glycolysis product can be used as it is or in a mixture with other polyol products for the obtaining of polyurethanes. In this

Table 1
ADHESIVE FORMULATIONS FOR WOOD

Assortment	Polyol quantity (g)	Neoprene NW[a] solution in toluene, quantity (g)	MDI quantity (g)	M_{Pol}/M_{MDI}	M_{NW}/M_{Pol}	M_{NW}/M_{MDI}
1	6	3	4.3	1.40	0.50	0.70
2	10.24	5.22	5.23	1.96	0.51	1.00
3	9.95	5	5.73	1.74	0.50	0.87
4	5.55	3	5.18	1.07	0.54	0.58
5	5.21	2.5	8.3	0.63	0.48	0.30
6	9.36	5.76	14.32	0.65	0.62	0.40

[a] The Neoprene NW solution in toluene has a concentration of 8.4%

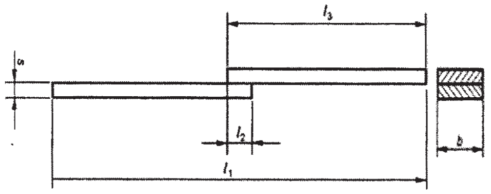


Fig. 3. Lap joint test pieces for shear stress strength determination
l_1 = total length test piece (150 ± 2) mm; b = width of the test piece (20 ± 0,2) mm; l_3 =length of a test piece (80 ± 2) mm;
s = thickness of a panel (5 ± 0,1) mm;
l_2 = length of the overlap (10 ± 0,2) mm

context, our aim has been to utilize directly the polyol oligomers for the obtaining of polyurethane adhesive and foams.

Polyurethane adhesives

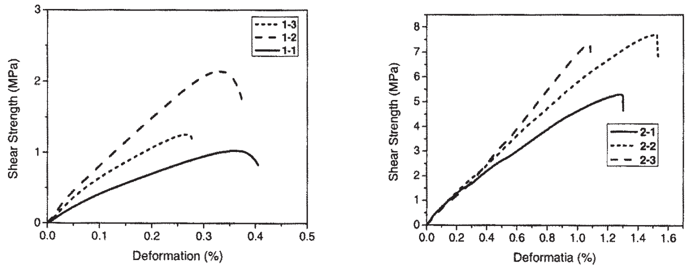
The molecular weights of the obtained polyols after PET glycolysis are well suited for the elaboration of polyurethane adhesives for polar surfaces [24]. Considering that the polyol component presents an important part in the manufacturing cost of the adhesive, we have elaborated different assortments containing the polyol, MDI and NW dissolved in toluene. In table 1, six adhesive formulations for wood are presented.

The realization of different polyurethane adhesive bi-component formulations involved several aspects:

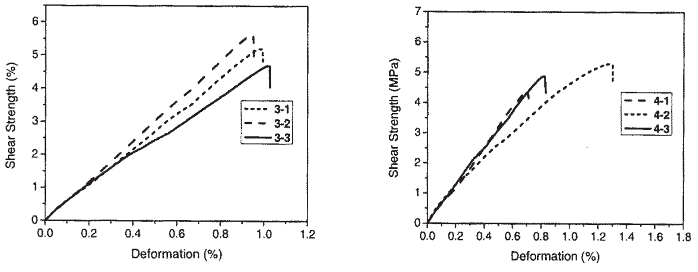
- premixing of the PET glycolysis product with the neoprene solution until homogenization;
- the addition of the MDI component and continuous stirring for easy applications;
- the application of the adhesive on the surface of the wood test pieces by brush technique.

The six adhesive formulations have been tested in order to determine the tensile shear strength of lap joints according to the EN 205:2003 (Adhesives – Wood adhesives for non-structural applications – Determination of tensile shear strength of lap joints). The wood (*Fagus sylvatica L.*) test pieces were cut to the standardized (EN 205:2003) dimensions and bonded as presented in figure 3.

In figure 4 are presented the shear stress resistances of the tested formulations which represent one most crucial parameter of adhesives quality.

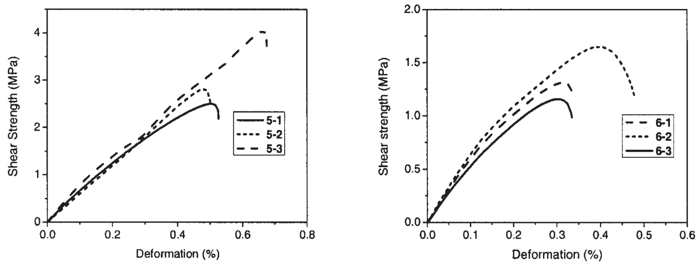


Test piece no.	*Shear strength [MPa]*	*Test piece no.*	*Shear strength [MPa]*
1-1	*1.25*	2-1	*5.29*
1-2	*1.02*	2-2	*7.69*
1-3	*2.14*	2-3	*7.31*



Test piece no.	*Shear strength [MPa]*	*Test piece no.*	*Shear strength [MPa]*
3-1	*5.21*	4-1	*4.41*
3-2	*5.62*	4-2	*5.29*
3-3	*4.70*	4-3	*4.88*

Fig. 4. Shear strength of the polyurethane adhesive formulations



Test piece no.	*Shear strength [MPa]*	*Test piece no.*	*Shear strength [MPa]*
5-1	*2.50*	6-1	*1.31*
5-2	*2.80*	6-2	*1.65*
5-3	*4.06*	6-3	*1.16*

Fig. 4 (cont.). Shear strength of the polyurethane adhesive formulations

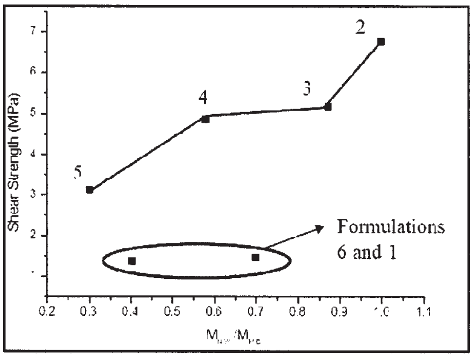


Fig. 5. Shear strength variation depending on the NW / MDI weight ratio

Table 2
POLYURETHANE FOAM CHARACTERISTICS

	Characteristic	**Test method**	**Unit**	**Obtained Values**
1	Apparent density , ρ_a	SR EN 1602:2013	kg/m^3	112
2	Thermal conductivity (λ): - at 23^{0}C - at 10^{0}C	SR EN 12667:2002	W/mK	 0.0442 0.0412
3	Thermal resistance (R), at a nominal thickness of 50 mm: - at 23^{0}C - at 10^{0}C	SR EN 12667:2002	m^{2}K/W	 1.13 1.21
4	Compressive stress at 10% deformation (σ_{10})*	SR EN 826:2013	kPa	651
5	Short-term (24 h) water absorption by total immersion	SR EN 12087:2013	%	3.4
6	Short-term (24 h) water absorption by partial immersion	SR EN 1609:2013	kg/m^2	0.6
7	Determination of dimension stability under specified condition of temperature and humidity: •-20^{0}C, 48 h $\Delta\varepsilon_l$ (length) $\Delta\varepsilon_b$ (width) $\Delta\varepsilon_d$ (thickness) •+60^{0}C and 90%RH, 48 h $\Delta\varepsilon_l$ (length) $\Delta\varepsilon_b$ (width) $\Delta\varepsilon_d$ (thickness)	SR EN 1604:2013	%	 +0.06 +0.01 -0.04 +0.05 -0.08 +0.26
8	Deformation under specified conditions of compression and temperature (20kPa, 80^{0}C, 48 h)	SR EN 1605:2013	%	0.94%

Considering the polyol mass constant, the determining parameter for the shear stress resistance was the ratio between the elastomer and MDI. We have calculated the weight ratio M_{POL}/M_{MDI} and M_{NW}/M_{POL}, from which the ratio M_{NW}/M_{MDI} was also determined. Thus, for the samples 2 to 5, a higher elastomer to MDI ratio afforded an increased shear stress resistance (fig. 5). However, for samples 1 and 6 which present lower shear stress resistance this observation is not consistent.

Commercial polyurethane wood adhesives must be able to fill the gap between the bonded pieces, realize a good interaction with the interfaces and present adequate mechanical properties. Thus, the adhesive must have good flow and wetting properties. The shear stress values obtained for the adhesive formulation 2 recommend it for as wood adhesive.

Polyurethane foams

For the realization of rigid polyurethane foams, we have used PETOL PA-500-5D and castor oil in conjunction with the polyol resulted from the PET glycolysis. The formulation consisted in the realization of component A: 273 g Polyol, 34.1 g PA (PETOL PA 500-5D), 34.1 g castor oil and 2 mL water, well homogenized. The component B consisted in 324 g MDI which was added over component A and stirred, creaming time 1 min , followed by the rising stage. The images of the obtained polyurethane foam are presented in figure 6.

In table 2 are presented the characteristics of the obtained rigid in situ polyurethane foam.

All the characteristics of the foam recommend its utilization as rigid insulating material with multiple applications: wall insulation – both at the interior and exterior of the building, under-floor insulation, ceilings –

Fig.6. Sample of polyurethane foam (a) and test piece for determination of thermal conductivity (b)

including flat roofs, basement and main floors insulation and other insulation application were good mechanical properties are required.

Conclusions

The aim of this study was to present the obtaining of new products with added value through facile synthesis approach starting from post-consumer poly(ethylene terephtalate) (PET) bottles. The depolymerization of PET in a microwave reactor allowed the use of diethylene glycol (DEG) and catalyst (zinc acetate) in reduced amounts compared with conventional methods. The glycolysis products were used as such in order to develop new formulations for polyurethane adhesives and foams. The adhesives mechanical properties were tested affording samples with tensile shear resistance suitable for commercialization. The polyurethane foams testing confirmed the obtaining of rigid structure with good thermal insulation properties.

The manufacturing processes involved one step reaction without any side products and lower energy consumption through the use of microwaves, coming in the environmental and economic benefit through the efficient alternative of PET recovery.

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