Polyester-ether Polyols for Rigid Polyurethane Foams, Prepared from PET Wastes by a *Clean* Method

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Polyester-ether polyols were prepared by a clean method, consisting of PET wastes glycolysis with common diols (diethylene glycol and a mixture diethylene gycol/ dipropylene glycol) and a diol derived from biomass (isosorbide) followed by mono-esterification of the glycolyzed products with phthalic anhydride and subsequent propoxylation, under relatively mild conditions. The polyester-ether polyols were characterized by chemical methods, dynamic viscosity measurements, gas chromatography and ^{1}H-MNR spectroscopy. Experiments, conducted in order to test the polyester-ether polyols in rigid polyurethane (PUR) foams formation, showed that the chemical composition of the experimental polyester-ether polyols is fully suitable for reaction with di-isocyanate. The physico-mechanical and flame retardant properties of PUR foams, prepared by using the experimental polyester-ether polyols up to 30% wt. of the polyol component in the foam formulations, were at least similar to the properties of the foam obtained from PET wastes by classical recycling methods. The synthesis method is in agreement with the principles of clean technologies and green chemistry, in the sense that no by-products and no wastes results.

Keywords: clean procedure; PET wastes; polyester-ether polyols; NMR spectroscopy; rigid polyurethane foams

Clean technologies are, according to Clean Edge [1], *processes that dramatically reduce the use of natural resources, and cut or eliminate emissions and wastes.* This can be expressed as efficient recycling of waste to produce valuable materials, finding renewable sources as alternative to the classical feedstocks solution and maximizing the amount of raw material that ends up in the product [2]. In this framework, increased scientific interest is paid to the development of efficient recycling method of polyethylene terephtalate wastes. This polymer found a widespread application owing to its superior thermal and chemical resistance but, because of its non-biodegradability, huge amounts of wastes are produced [3]. According to the principles of sustainable development, chemical recycling is the most adequate technique for PET. This method allows controlled scission of the polymer chain with formation of monomers which can be re-used either in the production of the PET polymer or as building blocks to generate other value-added products [4]. Moreover, the backbone of the PET polymer can be structurally modified using suitable co-monomers, permitting control of the targeted properties of the resulting oligoesters [5,6]. An example from this point of view is the synthesis of polyester polyols *via* PET glycolysis with various glycols [7-11]. These polyols were used to produce polyurethane foams, but they show some drawbacks, namely the tendency to precipitate when stored at ambient temperature and also the high content of free low molecular weight glycols, which leads to the formation of irregular three-dimensional networks. To overcome such problems, there were developed procedures which involve the esterification of the resulting glycolysis products with dicarboxylic aliphatic/aromatic acids or their derivatives in order to avoid the crystallization and removal by vacuum distillation at low temperature of the free glycol [12,13]. However, in general these procedures involve high reaction temperatures (240-250°C), long enough reaction time (about 6-8 h) and formation of by-products, such as: methanol, water or glycols, whose removal from the reaction system raise serious separation and recovery problems.

The final properties of the polyurethanes are dependent on the chemical structure of the components, therefore tailoring the synthesis is an effective way to access the desired properties for a particular application. In this context, isosorbide (IS, 1,4:3,6 –dianhydrosorbitol) is of particular interest since it possess a rigid structure suitable for the design of rigid polyurethane foams [14]. In addition, IS is non-toxic and it is isolated from biomass, i.e. it is isolated from cereals starch *via* enzymatic and chemical processes. Therefore, the use of this diol is well fitted in the context of developing environmentally friendly chemical reactions where, the use of bio-based materials is of great relevance representing an alternative to petrochemical raw materials which become limited.

The purpose of the herein described research is to address the issue of developing a *clean* synthetic strategy for production of some aromatic polyester-ether polyols, suitable for production of polyurethane foams. We developed a procedure which is economical in terms of energy consumption and does not produce any waste,[15] in contrast to the existing conventional similar technologies [6]. This is based upon use of PET waste as starting material for obtaining polyols with certain properties under mild reaction conditions without releasing any by-products and residues. We also describe preliminary studies towards

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** email: em_duldner@yahoo.com; Phone: (+40)21 315 32 99; emerik_bartha@yahoo.com; Phone: (+40)21 316 79 00* use of isosorbide, a diol derived from biomass, for the preparation of polyurethane rigid foams. The isosorbide-based polyol chemical structure contains rigid structural units formed by esterification of this diol with aromatic dicarboxylic acids. This has been interpreted through investigations of the physico-mechanical and thermal properties of the resulting rigid polyurethane foams prepared therefrom.

Experimental part

Synthesis of functionalized oligoterephthalate structures

Materials

Post-consumer PET waste from bottles in flakes form (longitudinal dimension 6-8 mm), washed with clean water and dried at 100°C for 5 h with intrinsic viscosity (according to ASTM D4603) of 0.77 dL/g, were used for the degradation process. Diethylene Glycol (DEG), Dipropylene Glycol (DPG) were purchased from Merck, and used without purification. Propylene oxide (PO) was obtained from OLTCHIM SA, and used as it was received. Phthalic Anhydride (PA), analytical grade was purchased from Reactivul-S.A., Romania. Titanium (IV) i-propoxide (TTP), 1,4-diazabicyclo-[2.2.2]-octane (DABCO) and *N,N*-dimethylcyclohexylamine (DMCHA) catalysts were used as received.

Synthesis methods

PET glycolysis and subsequent monoesterification reactions were conducted in a a stainless steel polycondensation reactor of 1000 cm^3 capacity, fitted with electrically heating jacket, temperature controller, anchor stirrer with 60-70 rpm, nitrogen inlet, manometer and reflux condenser connected to a distillate collecting vessel. The alkoxylation reaction was conducted in a stainless steel polycondensation reactor of 1300 cm^3 capacity, suitable for reactions with alkylene oxides, maximal working pressure 10 atm, equipped with heating jacket, inside water cooling serpentine, turbine stirrer with 6 pallets at 280-540 rpm, nitrogen inlet tube, pressure equalization valve, descendant condenser, temperature controller, manometer and a supply vessel for alkylene oxide of 1000 cm^3 capacity. All reactions were performed in melt.

Glycolysis

PET wastes were glycolysed with DEG, DEG/ DPG mixture and IS, at a molar ratio diols / PET of: 1.5-2:1, in the presence of TTP catalyst at 190-220°C, atmospheric pressure under N_2 atmosphere under total reflux of glycols. The catalyst loading is reported to 0.1 % w. of PET content. The running time was from 3 and 4 h, respectively, in the case of PET glycolysis with isosorbide. For the synthesis of the benchmark polyester-eter polyol (PB), PET wastes were glycolysed in the same conditions using DEG/DPG mixture in a ratio which provided similar content of DEG/PG moieties as in the experimental P1 – P4 polyols structures.

Esterification

The resulting glycolysis products were partially esterified with phtalic anhydride (PA) using 1:1 PA/PET molar ratio. The reaction was conducted at temperatures between 120 - 140°C, under slow stream of nitrogen for 1 – 2 h. The reaction was monitored by acid number determination which corresponds to complete esterification of a single carboxylic group (by anhydride ring opening addition). The benchmark polyester-eter polyol synthesis was conducted to full esterification of the two carboxylic groups of the phthalic anhydride up to 240-250 °C over 5 - 6 h while water was distilled off.

Alkoxylation

The experimental reaction mixtures previously obtained were propoxylated with PO, at molar ratios PO/AF between 2- 4.2: 1, in the presence of DABCO or DMCHA catalysts, at a ratio of 0.5- 1% wt., based on esters mixture, at 110 - 120 °C temperature, 2 - 5 atm. pressure of PO, for about 2-3 h. The benchmark polyester-eter polyol was not subjected to propoxylation reaction.

Methods and techniques used to characterize the polyester-ether polyols

The Acid number (I_A) of the polyester-ether polyols was determined according to ASTMD-4662 -98 : Standard methods for testing raw materials for polyurethanes - Determination of acidity and alkalinity of polyols. The Hydroxyl number (I_{OH}) of the polyester-ether polyols was determined according to ASTM-D4274-05: Standard methods for testing raw materials for polyurethanes - Determination of hydroxyl number of polyols. For average molecular weight calculation, the end-groups method was used, adopting the values of acid number and hydroxyl number determined according to the above mentioned methods, without removal of free glycols. The water content (%) was determined by Karl - Fischer method, according to ASTM-D4672-05-Standard methods for testing raw materials for polyurethanes -Determination of water content of polyols. The free glycols content (% wt.) was determined by gas-chromatography of acetylated samples of poly – ester-ether polyols, on a Carlo Erba gas cromatograph, model 2450, with capillary quartz column filled with stationary phase methyl-phenyl silicone (5% phenyl). The dynamic viscosity of the polyols was determined according to ASTM-D4878-03- Standard methods for testing raw materisls for polyurethanes - Determination of polyols viscosity. ^{1}H-RMN spectra of the polyols and the samples processed by derivatization were recorded on a Varian Gemini 300 MHz with superconductor magnet and Bruker 500 spectrophotometer.

Polyester-ether polyols evaluation in rigid polyurethane foams formation

Preparation method

The behaviour of the polyester-ether polyols in the foaming process was evaluated according to the cup test method, free rise process, in a formulation for sandwich panel - discontinuous process of rigid polyurethane foam formation. The polyester-ether polyols P1, P2, P3, P4 and PB were tested using the following formula: Polyether polyol Petol PZ 400-5G - 50 pbw.; Polyester-ether polyol P1-P4 - 30 pbw.; Polyether polyol Petol PM 500-3F - 20 pbw.; Silicon surfactant Tegostab 8461 - 1.5 pbw.; *Tris*(chloropropyl)phosphate) flame retardant TCPP - 12 pbw. ; N,N-dimethyl cyclohexyl amine catalyst - 0.4 pbw.; *N,N*-dimethylethanol amine catalyst- 0.6 pbw.; Water- 3 pbw.; Blowing agent -pentafluorobutane/heptafluoro-propane HFC 365 mfc/227 ea - 20 pbw.; Crude MDI [4,42 - Methylenebis(phenyl isocyanate)] Index – 110.

The polyester-ether polyol P5 was tested using the following formula: Polyether polyol Petol PZ 400-4G - 50 pbw.; Polyester-ether polyol P5 - 30 pbw.; Petol PM 500-3F - 20 pbw.; Glycerol - 2 pbw.; Tegostab 8461 - 1.7 pbw.; TCPP- 15 pbw.; *N,N*-dimethylcyclohexyl amine - 0.8 pbw.; Water- 3 pbw.; HFC 365 mfc/227 ea: 20 pbw.; Crude MDI index : 110

Characterization

The following characteristics were determined: i) reaction mixture's reactivity; ii) physico -mechanical properties of foams (according to ISO845, ISO844, ISO1209 and ISO2796 standard determination methods); iii) fire reaction (according to ISO3582 standard determination method).

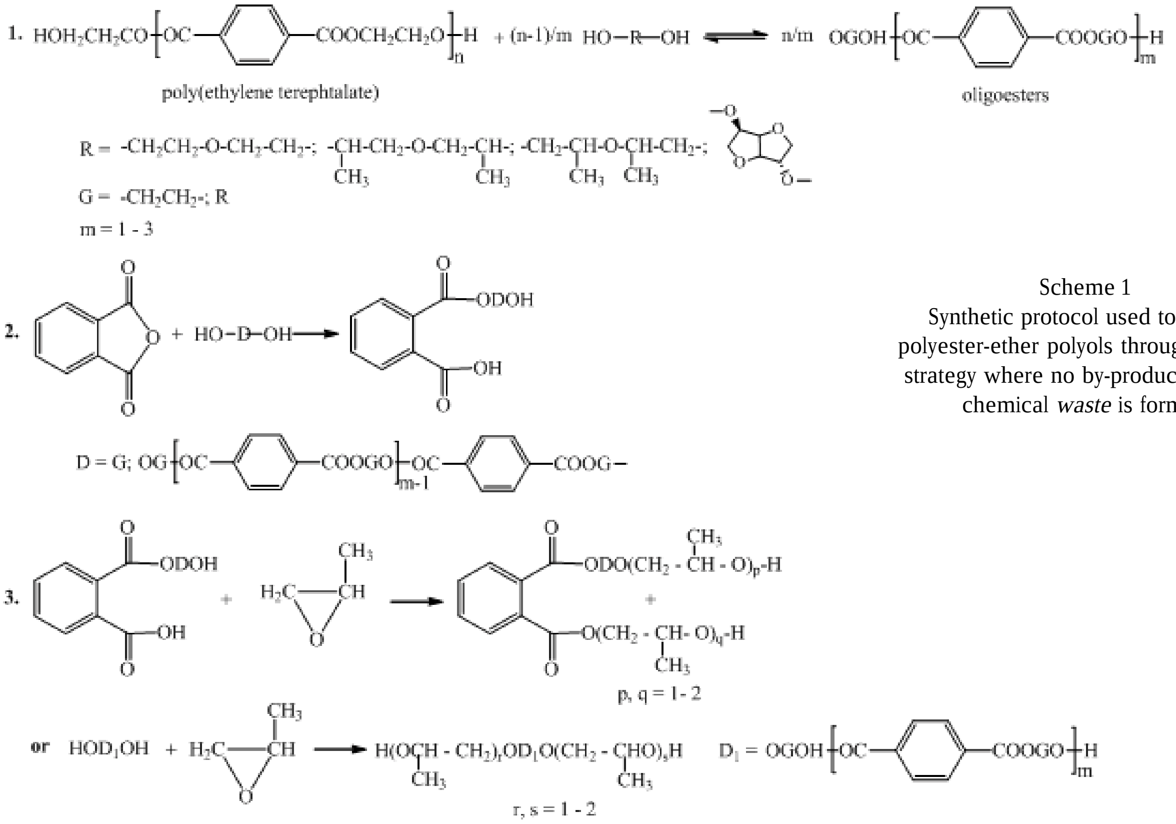
Results and discussions

The synthetic protocol is consistent with the green chemistry principles, namely the chemical recycling of PET waste to produce polyester-ether polyols following a synthetic strategy in which no by-product or other wastes are formed. The used experimental method (scheme 1) is a melt glycolysis-esterification-alkoxylation procedure starting with glycolysis of PET waste with aliphatic polyols or polyoxyalkylene glycols of low molecular weight (DEG, DPG, IS). The glycolytic destruction of PET is catalyzed by titanium (IV) isopropoxide at temperature ranging from 190 °C to maximum 220 °C, similar to the classical glycolysis procedure. The second step supposes partial esterification with aromatic anhydride of an aromatic polycarboxylic acid (PA), to achieve an acid number corresponding to complete esterification of a single carboxylic group. This reaction occurs in mild conditions (up to 140 °C, 1 – 2 h) in comparison with the classical reaction where, for a complete esterification on both carboxy groups, high temperature and long reaction time are required. The last step of the protocol consists in the alkoxylation of the reaction mixture with propylene oxide, in the presence of base catalysts (tertiary amines: DABCO, DMCHA) at 110 – 120 °C. This last step assures the full esterification of the carboxyl groups and, in some extend, the etherification of terminal hidroxyl groups.

Polyester-ether polyols characterization results

Physico-chemical properties of the polyester-ether polyols

The polyols physico-chemical characteristics are very important in the process of foams formation, as well as in determining the properties of the final polyurethane polymer [16]. The physico-chemical properties of the herein described polyester-ether polyols are presented in table 1.



Scheme 1
Synthetic protocol used to obtain polyester-ether polyols through a *clean* strategy where no by-product or other chemical *waste* is formed

Table 1
CHEMICAL COMPOSITION (REACTANTS RATIO) AND PHYSICO-CHEMICAL PROPERTIES OF THE HEREIN DESCRIBED POLYESTER-ETHER POLYOLS

Polyol code	Polyester-ether polyols composition Structural moieties deriving from:							Physical-Chemical Characteristics of Polyester-ether polyols							
	Dicarbox. arom. acids moles/1mol PET		Diols, moles/1mol PET					IA mg KOH/ g	IOH mg KOH/ g	Mn calc.	η, cP			Water cont. (KF^1), %	Free glycols low w. (GC^2) %
	TA*	PA	EG**	DEG	DPG	IS	PG***				25°C	50°C	70°C		
P 1	1	1	1	1.8	0	-	3.4	0,20	282	398	10272	-	-	-	-
P 2	1	1	1	2	0	-	3.9	0.28	320	351	2835	324	98	0.23	9.5
P 3	1	1	1	2	0	-	4.2	0.10	315	356	2757	298	95	0.10	9.8
P 4	1	1	1	1	1	-	3.0	0.25	316	355	3089	341	103	0.28	9.9
P 5	1	1	1	0	0	1.4	2.0	0.20	170	660	paste	36202	3436	0.35	-
PB	1	1	1	1.12	2.18	-	-	1.20	341	328	3040	407	103	0.25	21.5

*TA – terephthalic acid derived from PET; ** EG – ethylene glycol derived from PET; ***PG – 1,2 propylene gycol moieties from PO (propylene oxide) (calculated from the increased weight of the reaction mass); ^{1}Karl Fischer; ^{2}Gas chromatography

Analysis of the data reveals that the polyester-polyols, P1 - P5 obtained by the present sequence of chemical reactions display a lower acidity index when compared to PB obtained by traditional esterification procedure. This is an advantage over the classical recycling method since no negative effect on the foaming catalyst performance is produced alongside with a better hydrolytic stability of the polyester-eter polyols. A restrictive parameter in polyurethane foam technology is connected with the free glycol content which has to be as lower as possible. As can be seen in table 1, all polyols have similar OH number, around 300 mg KOH/g, which is in the range of regular polyols for rigid polyuretahne foams (250 - 400 mg KOH/ g). The polyols present low viscosity values which are very suited for polyurethane (PU) processing, values up to 15000 cP being accepted. The P1 – P4 polyester-ether polyols are liquids, whereas the one obtained by cleaving the PET wastes with isosorbide showed a paste aggregation state.

A thorough analysis of the chemical composition and physico-chemical properties of the obtained polyester-ether polyols provides the proof that the developed procedure is superior when compared to conventional protocol. In terms of economical efficiency, the herein proposed synthetic route requires lower temperature, shorter reaction time (3 h at 200°C for the glycolysis, similar to the classical method; 4 - 5 h at 120-140 °C for the subsequent steps *versus* 6 - 8 h at 240-250 °C in the classical procedure) and does not generate any byproducts. This is in agreement with the listed results which reveal that the use of propylene oxide produced polyols with lower acidity index and low free glycol content as compared to traditional methods (PB in table 1).

^{1}H-NMR spectra of polyester-polyols

The chemical composition of the reaction products was established by ^{1}H-NMR spectroscopy in deuterated chloroform. For the P2 polyester-ether polyol sample, the ^{1}H-NMR spectrum is shown in figure 1, a. Detailed analysis of the spectrum shows the formation of both ester and ether group polymers. The spectrum contains three characteristic chemical shifts for the aromatic protons in the area 8.1 – 7.4 ppm assigned to the aromatic benzene units of the monoester and polyester-ether polyols. The most deshielded signal was attributed to the terephthalic moiety, whereas the other two belong to the phthalic units. The upfield signals located between 1.3 – 1.0 ppm are assigned to the methyl protons of the propylene glycol and are observed as multiplets owing to tactic/isotactic orientation of these groups inside the dimer, trimer, etc. The spectrum is quite complicated, but one can distinguish the signals belonging to the aryl bound PG and DEG moieties at 5.3 and 4.5 ppm respectively, as well as the free glycols signal at 3.4 – 3.2 ppm, alongside with ethylene glycol signals of glycolized PET. Next, the multiplet located at 4.4 – 4.2 ppm was assigned as ArO—CH_2—CH(CH_3)—OH of the primary alcohol of the bonded propylene glycol, while the 5.3 - 5.2 ppm multiplet is assigned to the secondary alcohol group of the bonded propylene glycol, ArO—CH_2—CH(CH_3)—OH. The aryl-DEG characteristic signal is centered at around 4.5 ppm, whereas the ethylene glycol chemical shift is observed at 4.6 ppm. Correlation of the signals integration corresponding to methyl groups from PO moieties with that of the signals assigned to the aromatic protons from the phthalic units, allows the determination of the PO/ PA ratio as being 3.8, which is consistent with the calculated amount of reacted PO.

For improving the quality and suppressing the errors, the derivatization of the obtained polyester-ether polyols with acetic anhydride was performed. In this case (fig. 1, b) a better separation of the proton chemical shifts was observed that allows eloquent assignment of the structural features. The acetyl protons (OAc) are observed at 2.0 ppm, while the chemical shifts at 5.4 – 4.1 ppm are attributed to the ester functionalized PG and DEG (fig. 1, b). The aromatic protons resonate in the expected region, i.e. as three large deshielded signals assigned as described above. The multiplets ascribed to the acetylated hydroxyl groups are now clearly separated and present downfield shifts for the aromatic bonded groups (fig.1,b for the chemical assignment). By comparing the signal of the aromatic protons with the acetyl-functionalized hydroxyl groups, it is possible to assume a content of 1.87 hydroxyl group per aromatic unit. Detailed analysis of the signal integrations allows determination of the embedded propylene glycol in ester and ether bond as being 25 : 75 %. The primary/ secondary hydroxyl group ratio was determined to be 2,44 to 1 with 15 % (mol) content of free propylene glycol from the total PO moieties.

For the P5 polyester-ether sample, when the glycolysis of PET waste was performed with isosorbide, the ^{1}H-NMR spectrum of the reaction product after monoesterification with phtalic anhydride followed by esterification/ etherification with propylene oxide is shown in figure 2 a. The multiplets located between 8.0 - 7.5 ppm region are indicative of the benzene groups from the embedded phthalic units in the polyester - ether polymer. As previously

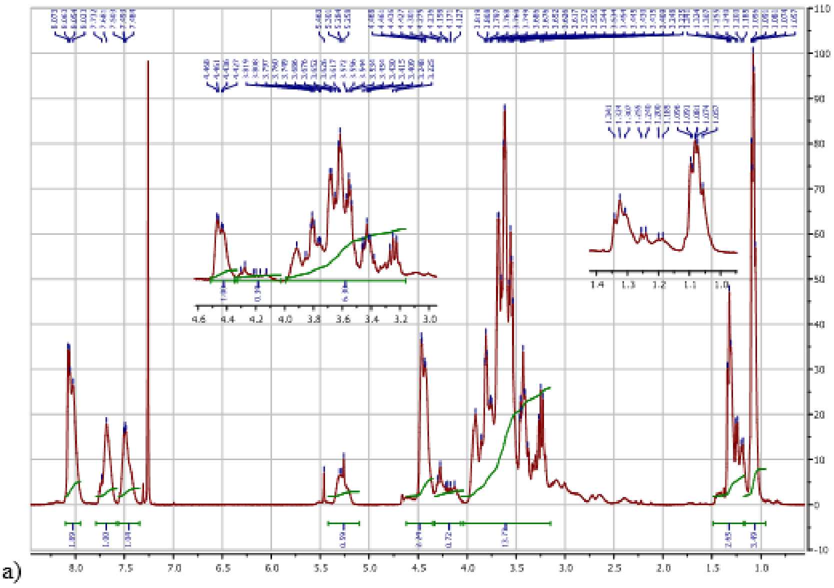


Fig. 1. ^{1}H-NMR spectra of P2 polyester-ether polyol, as such (a)

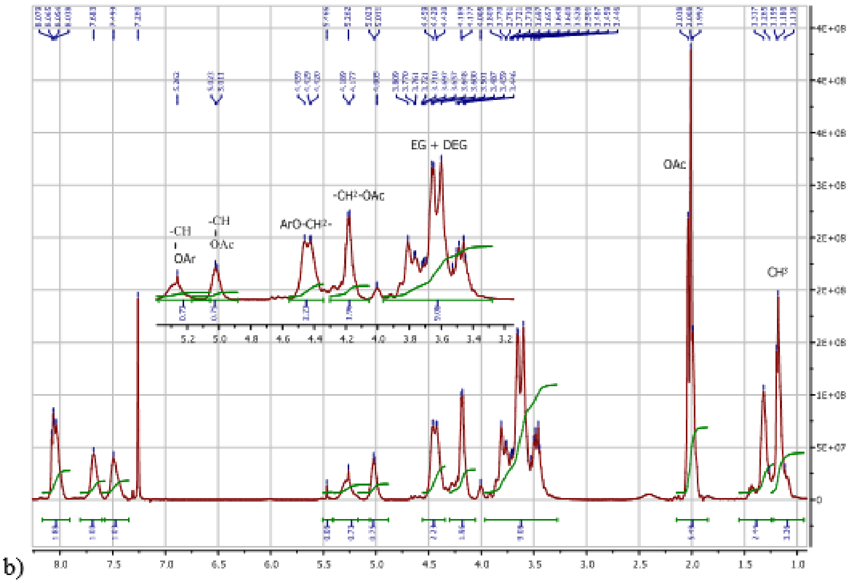


Fig. 1. ^{1}H-NMR spectra of P2 polyester-ether polyol, acetilated (b)

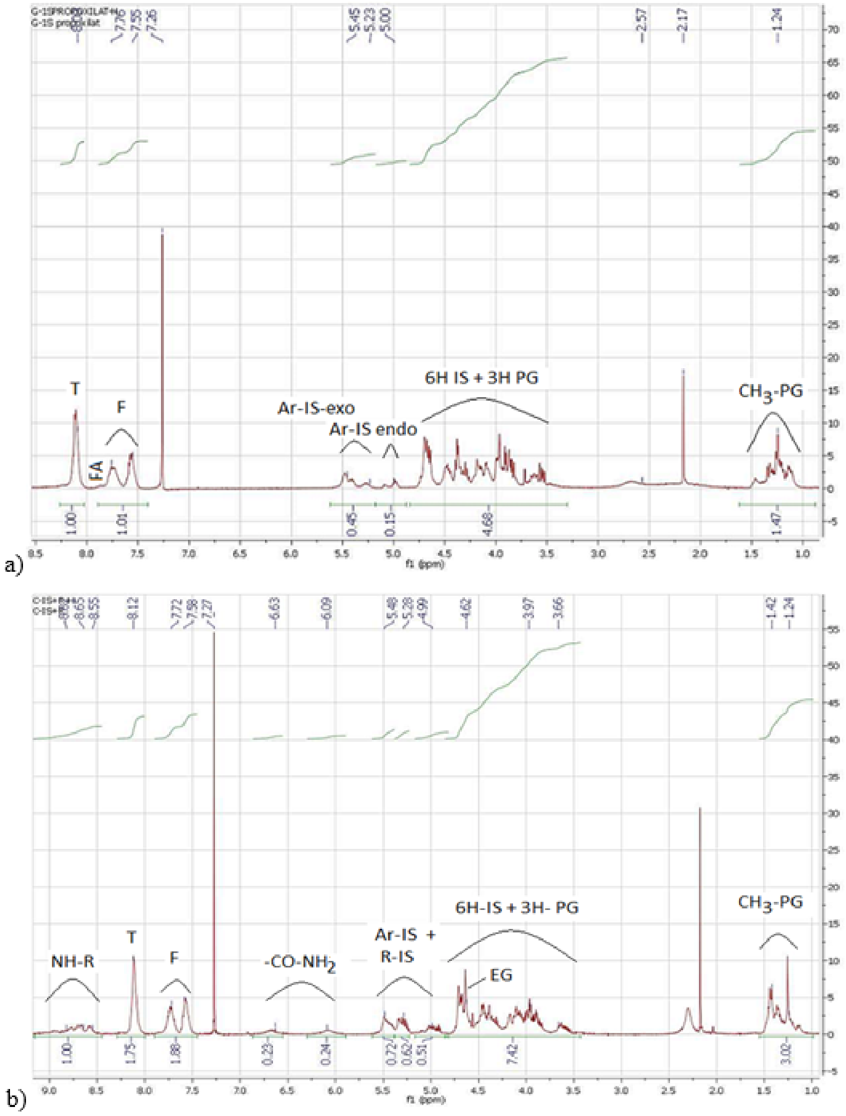
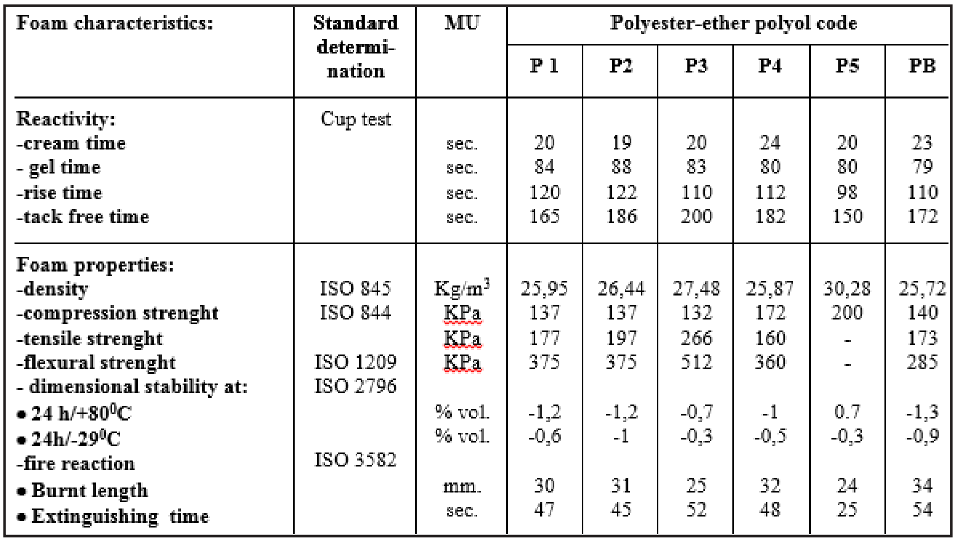


Fig. 2. ^{1}H-NMR spectra of experimental polyester-polyol P5, as such (a) and derivatized with trichloroacetyl isocyanate $Cl_3C–CO–N=C=O$ (b)

described, the methyl protons of the propylene glycol units were observed around 1.2 ppm. Correlation of the signals integration corresponding to methyl groups from PO moieties with that of the signals assigned to aromatic protons from the phthalic units, allows the determination of the PO/ PA ratio as being 2.1. The assignment of the methyne protons of the isosorbide and propylene glycol are shown in figure 2a. The *endo* and *exo* reacted hydroxyl groups of the isosorbide diol are downfield shifted between 5.4 and 4.9 ppm, as a consequence of their ligation to the aromatic groups and in accordance with literature reports [17,18]. The ester/ether embedded glycol ratio is 47:53 %. Starting from the terephtalic acid (noted T on the spectrum shown in fig. 2,a), considered as 1 mol, the resulting integral per proton is equal to 0.25. Analysis of the integrals of the exo/endo isosorbide protons (0.3 in the spectrum) reveals that 1.2 moles of isosorbide is present as Ar-IS. Taking into account the amount of used isosorbide for PET glycolysis

Table 2

PHYSICO-MECHANICAL PROPERTIES AND FIRE REACTION OF THE POLYURETHANE RIGID FOAMS



Foam characteristics:	Standard determi-nation	MU	Polyester-ether polyol code					
			P 1	P2	P3	P4	P5	PB
Reactivity:	Cup test							
-cream time		sec.	20	19	20	24	20	23
- gel time		sec.	84	88	83	80	80	79
-rise time		sec.	120	122	110	112	98	110
-tack free time		sec.	165	186	200	182	150	172
Foam properties:								
-density	ISO 845	Kg/m^3	25,95	26,44	27,48	25,87	30,28	25,72
-compression strenght	ISO 844	KPa	137	137	132	172	200	140
-tensile strenght		KPa	177	197	266	160	-	173
-flexural strenght	ISO 1209	KPa	375	375	512	360	-	285
- dimensional stability at:	ISO 2796							
• 24 h/+80^{0}C		% vol.	-1,2	-1,2	-0,7	-1	0.7	-1,3
• 24h/-29^{0}C		% vol.	-0,6	-1	-0,3	-0,5	-0,3	-0,9
-fire reaction	ISO 3582							
• Burnt length		mm.	30	31	25	32	24	34
• Extinguishing time		sec.	47	45	52	48	25	54

(1.4 mol) and the Ar-IS formed according to the ^{1}H-NMR spectroscopy (1.2 mol), a conversion of 86 % was determined for the aromatic-bonded isosorbide moieties. Consequently, the rest of 14 % can be in the form of free diol or eterified diol by self-reaction or with PO.

The interpretation of the ^{1}H-NMR spectrum was confirmed by derivatizaton with trichloroacetyl isocyanate [19], valuable agent in the assignment of the resonance signal of the free OH groups (fig. 2, b) This derivatizing reagent forms the corresponding urethane when reacted with hydroxyl groups and amide, respectively, when water is present, with characteristic resonances for the first compounds around 8 – 9 ppm. The free hydroxyl groups were found to be 1.1 per aromatic unit. The ratio of secondary OH groups from IS and PG per aromatic unit ratio, found to be 1.2, leads to the conclusion that the free OH groups are substantially all secondary. The presence of water in the reaction mixture is confirmed by the characteristic amide protons at 6.1 and 6.6 ppm, respectively. Detailed analysis of the signal integrations allows determination of the ratio of free OH groups from isosorbide per OH groups of isosorbide esterified with aromatic units as being around 1.1.

Characteritics of the polyurethane rigid foams

The characterization results of the polyuretane foams are listed in table 2. The structure-property of the polyols determines the performance of the polyurethane (PU) rigid foams. The characteristics of the PU foams are presented for P1 to P5 polyols and compared to PB-polyol obtaind by conventional procedure of PET recycling. The foam deriving from EG, DEG and DPG (P1 to P4) showed a density of around 25 kg/m^3, similar to the normal value for rigid sandwich-panel foams formulation. In the case of isosorbide-based polyol containing foam, a small increase of the density to 30 kg/m^{3}was observed. The preparation of the foams revealed also that all investigated polyester-ether polyols are compatible with the common polyether-polyols used for PUR foams, forming together stable and homogenous mixtures. The physico-mechanical and flame retardant properties of the resulting rigid polyurethane foams up to 30% wt. polyester-ether polyols content were at least similar to the properties of the foams obtained from PET wastes by classical recycling methods (PB). The polyol containing isosorbide leads to improvement of the compression strength, dimensional stability and fire reaction of the resulting PUR foam.

Conclusions

Polyester-ether polyols were prepared by a *clean* method, consisting of PET wastes glycolysis with common diols (diethylene glycol and a mixture diethylene glycol / dipropylene glycol), monoesterification of the products with phthalic anhydride, followed by propoxylation, under relatively mild conditions**.** Furthermore, the process was conducted towards green chemistry by using for cleaving the PET chain a nontoxic diol of bio-provenience, such as isosorbide. The polyester-ether polyols were characterized by chemical methods, dynamic viscosity measurements, gas chromatography and ^{1}H-NMR spectroscopy. The results showed that liquid polyester-ether polyols with convenient dynamic viscosities and low content of free glycols were obtained, when using diethylene glycol and dipropylene glycol as cleaving reagents, while the polyester-eter polyol obtained by cleaving PET wastes with isosorbide showed a paste agregation state and a low content of free low molecular weight glycols. ^{1}HNMR spectra provided information concerning the products composition, allowing assumptions regarding the chemical reactions development.

Experiments, conducted in order to test the polyester-ether polyols in polyurethane rigid foams formation, showed that all were compatible with the common polyether-polyols for PUR foams, forming together stable and homogenous mixtures. The physico-mechanical and flame retardant properties of the obtained rigid polyurethane foams with up to 30% wt. of the polyol component are better or at least similar to the properties of the foams obtained from PET wastes by classical recycling methods. The polyol containing isosorbide led to improvement of the physico-mechanical and flame retardant properties of the PUR foam. The significance of this research work is given by the fact that, a clean procedure was found for the synthesis of polyester-ether polyols from PET wastes, useful for prepapation of rigid polyurethane foams, whereby no by-products or waste are produced.

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