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A STUDY ON THE CHEMICAL REACTIONS USED IN THE SYNTHESIS OF POLYESTER POLYOL USING WITH RECYCLED RIGID POLYURETHANE FOAM WASTE

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ABSTRACT

Polyester-ether polyols is prepared using a clean process consisting of PET waste glycolysis with traditional diols (diethylene glycol and diethylene gycol / dipropylene glycol mixture) and biomass-derived diol (isosorbide) accompanied by mono-esterification of glycolyzed materials with phthalic anhydride and eventual propoxylation under reasonably mild conditions. Polyester-ether polyols have been described by chemical processes, realistic viscosity tests, gas chromatography and 1 H-MNR spectroscopy. Experiments to test polyester-ether polyols in rigid polyurethane (PUR) foam formation have shown that the chemical structure of experimental polyester-ether polyols is completely appropriate for reaction with di-isocyanate. Physico-mechanical and flame retardant properties of PUR foams, prepared using experimental polyester-ether polyols up to 30% wt. The polyol portion in foam formulations was at least close to the properties of foam generated from PET waste by traditional recycling methods. The method of synthesis is compatible with the principles of cleaner technology and green chemistry, in that no by-products and no waste are generated.

Keywords: *clean procedure; polyester-ether polyols; rigid polyurethane foams.*

INTRODUCTION

Green technologies are, according to Green Edge[1], systems that significantly minimize the usage of natural capital and reduce or remove pollution and waste. This can be described as effective processing of waste for the manufacture of useful products, seeking green sources as an alternative to traditional feedstock methods and optimizing the amount of raw material that ends up in the product[2]. In this context, expanded research attention is given to the creation of an appropriate processing system for polyethylene terephthalate waste. This polymer has been commonly used due to its superior thermal and chemical tolerance, but due to its non-biodegradability, tremendous quantities of waste are produced[3]. According to the ideals of sustainable growth, chemical processing is the most suitable strategy for Cat. This approach enables the regulated scission of the polymer chain with the creation of monomers, which can be re-used either in the manufacture of PET polymers or as building blocks for the generation of other value-added products[4]. In addition, the backbone of the PET polymer may be structurally changed using sufficient co-monomers, enabling the target properties of the resulting oligoesters to be controlled[5,6]. The synthesis of polyester polyols by PET glycolysis with different glycols [7-11] is an example from this point of view. These polyols have been used to manufacture polyurethane foams, but they have certain disadvantages, namely the propensity to precipitate while stored at ambient temperature and also the high free low molecular weight glycol material, which contributes to the creation of abnormal three-dimensional networks. In order to overcome these problems, procedures have been established which require 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]. In general, however, these procedures include elevated reaction temperatures (240-250 ° C), long enough reaction time (approximately 6-8 h) and the production of by-products such as methanol, water or glycols, the removal of which poses severe separation and recovery issues. The final properties of polyurethanes rely on the chemical composition of the materials, which is why synthesizing is an successful way of obtaining the necessary properties for a specific application. In this case, isosorbide (IS, 1,4:3,6 – dianhydrosorbitol) is of special interest because it has a rigid structure appropriate for the construction of rigid polyurethane foams[14]. In addition, IS is non-toxic and is extracted from biomass, i.e. extracted from cereal starch via enzymatic and chemical processes. The usage of this diol is also well adapted to the production of environmentally sustainable chemical reactions, where the use of bio-based materials is of considerable significance as an alternative to the existing petrochemical raw materials. The goal of the research mentioned herein is to address the issue of developing a clean synthetic strategy for the production of some aromatic polyester-ether polyols suitable for the production of polyurethane foams. We have established a technology that is economical in terms of energy use and does not generate any waste as compared to current traditional related technologies. This is focused on the usage of PET waste as starting material for the processing of polyols with some properties under moderate reaction conditions without the release of any by-products and residues. Preliminary research on the use of isosorbide, a biomass-derived diol, for the preparation of rigid polyurethane foams are also identified. The isosorbide-based polyol chemical structure comprises rigid structural units formed by the esterification of this diol with aromatic dicarboxylic acids. This was defined by studying the physico-mechanical and thermal properties of the subsequent rigid polyurethane foams.

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 100o 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,Ndimethylcyclohexylamine (DMCHA) catalysts were used as received.

Synthesis methods

PET glycolysis and corresponding monoesterification reactions were performed in a stainless steel polycondensation reactor with a capacity of 1000 cm3, equipped with an electrical heating vest, temperature controller, 60-70 rpm anchor stirrer, nitrogen inlet, manometer and reflux condenser connected to a distillate collecting tank. The alkoxylation reaction was conducted in a stainless steel polycondensation reactor with a capacity of 1300 cm3, ideal for reactions with alkyl oxides, a maximum working pressure of 10 atm, fitted with a heating vest, inside water cooling serpentine, turbine stirrer with 6 pallets at 280-540 rpm, nitrogen inlet hose, pressure equalization mechanism, descent condenser, temperature monitor, manomete. Both reactions have been melted.

Glycol sis

PET waste was glycolyzed with DEG, DEG / DPG mixture and IS, at a molar ratio of diols / PET of: 1.5-2:1, in the presence of TTP catalyst at 190-220 ° C, air pressure under N2 atmosphere under absolute glycol reflux. Loading of the catalyst is stated to be 0.1 percent w. Of the material of PET. In the case of PET glycolysis with isosorbide, the running period was 3 and 4 h, respectively. For the synthesis of the benchmark polyester-eter polyol (PB), PET waste was glycolyzed under the same conditions using the DEG / DPG mixture in a ratio which produced similar content of DEG / PG moieties as in the experimental P1 – P4 polyol structures.

Esterification

The resulting glycolysis products were partly esterified with phthalic anhydride (PA) using a molar ratio of 1:1 PA / PET. The reaction was performed at temperatures between 120-140 ° C, with a sluggish nitrogen flow of 1-2 h. The reaction was monitored by the calculation of the number of acids corresponding to the full esterification of a single carboxylic group (additional opening of the anhydride ring). The comparison polyester-ander polyol synthesis was performed to completely esterify the two carboxylic groups of phthalic anhydride up to 240-250 ° C over 5-6 h when the water was purified.

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 polyesterether polyols

Acid amount (IA) of polyester-ether polyols was calculated in compliance with ASTMD-4662-98: Normal methods for measuring polyurethane raw materials-Determination of acidity and alkalinity of polyols. Hydroxyl number (IOH) of polyester-ether polyols was calculated in compliance with ASTM-D4274-05: Normal methods for measuring polyurethane raw materials-Determination of the hydroxyl number of polyols. For the measurement of the average molecular weight, the end-group approach was used to follow the values of the number of acids and the number of hydroxyls calculated in compliance with the above methods, without the elimination of free glycols. The water content (percent) was calculated by Karl-Fischer system according to ASTM-D4672-05-Standard methods for measuring polyurethane raw materials-Determination of the water content of polyols. The free glycol content (percent wt.) was measured by gas-chromatography of acetylated poly-ester-ether polyol samples, on a Carlo Erba gas chromatograph, model 2450, with a capillary quartz column packed with stationary phase methyl-phenyl silicone (5 per cent phenyl). Dynamic viscosity of polyols was calculated in compliance with ASTM-D4878-03-Standard methods for evaluating raw material for polyurethanes-Determination of viscosity of polyols. 1 H-RMN spectra of polyols and samples processed by derivation were reported on a Varian Gemini 300 MHz with a superconductor magnet and a Bruker 500 spectrophotometer.

Polyester-ether polyols evaluation in rigid polyurethane foams formation

Preparation method

The behavior 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/heptafluoropropane 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

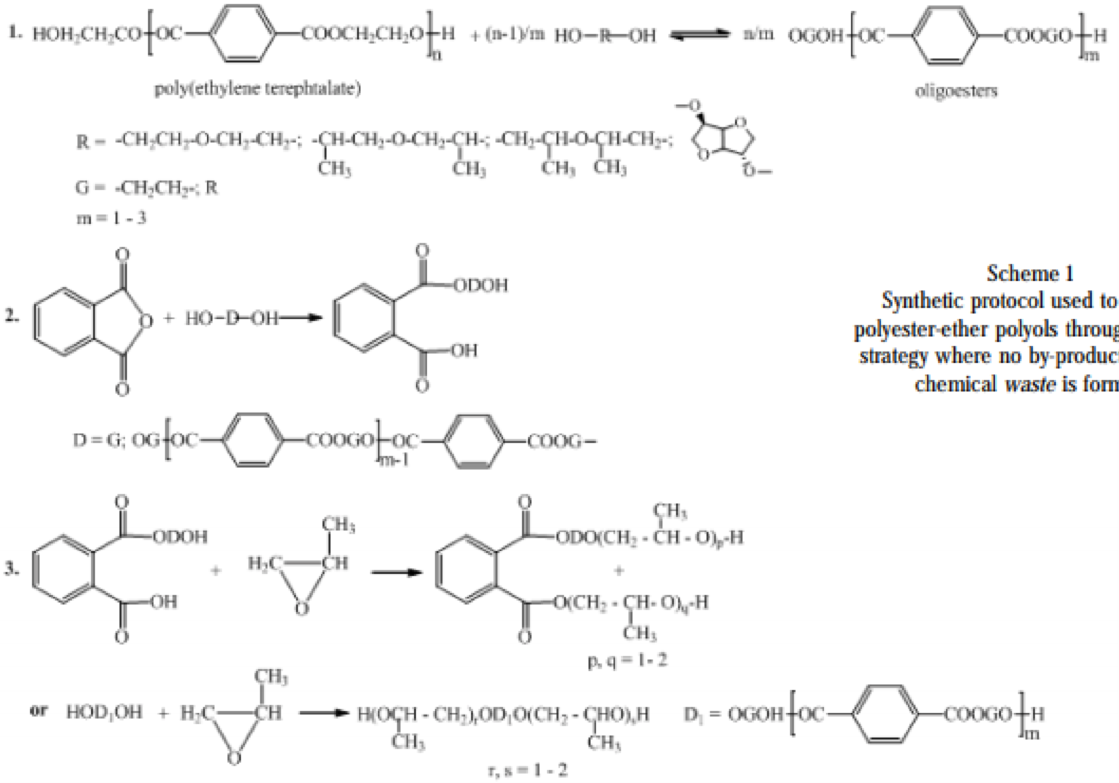
The following characteristics were determined: i) reaction mixture's reactivity; ii) physico - mechanical properties of foams (according to ISO845, ISO844, ISO1209 and ISO2796 standard determination methods); iii) fire reaction (according to ISO3582 standard determination method).

Results and discussions

The synthetic procedure is compatible with the ideals of green chemistry, namely the chemical recycling of PET waste for the manufacture of polyester-ether polyols adopting a synthetic technique under which no by-product or other waste is generated. The experimental process used (scheme 1) is the melt-glycolysis-esterification-alkoxylation technique, beginning with the glycolysis of PET waste with aliphatic polyols or low molecular weight polyoxyalkylene glycols (DEG, DPG, IS). The glycolytic degradation of PET is catalyzed by titanium (IV) isopropoxide at temperatures varying from 190 ° C to a maximum of 220 ° C, close to the traditional glycolysis technique. The second stage requires a partial esterification with aromatic anhydride of aromatic polycarboxylic acid (PA) to obtain an acid number corresponding to the full esterification of a single carboxylic group. This reaction occurs in mild conditions (up to 140 ° C, 1 – 2 h) compared to classical reactions where high temperature and long reaction time are needed for full esterification in both carboxy classes. The last stage of the process is 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 guarantees the total esterification of the carboxyl groups and, to some degree, the etherification of the terminal hydroxyl groups.

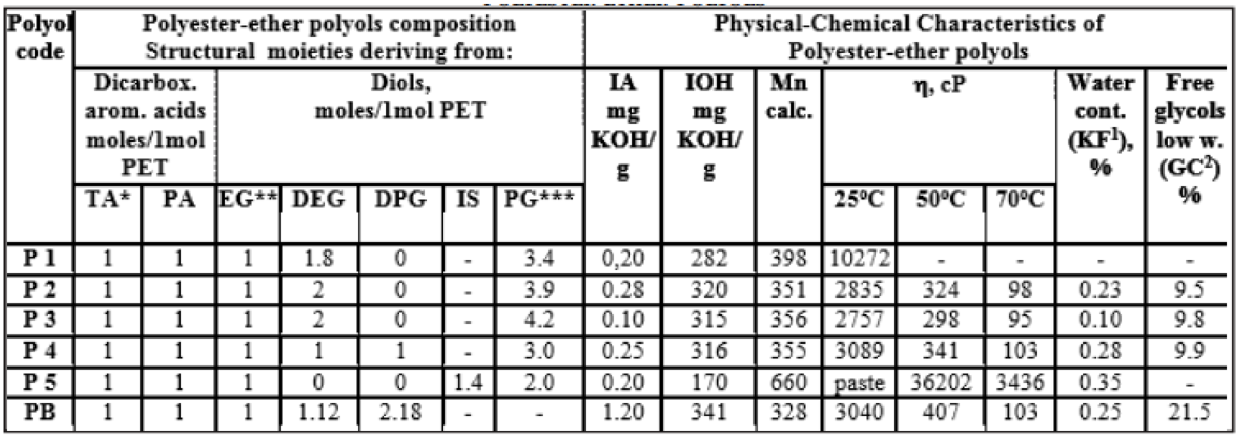
Polyester-ether polyols characterization results

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

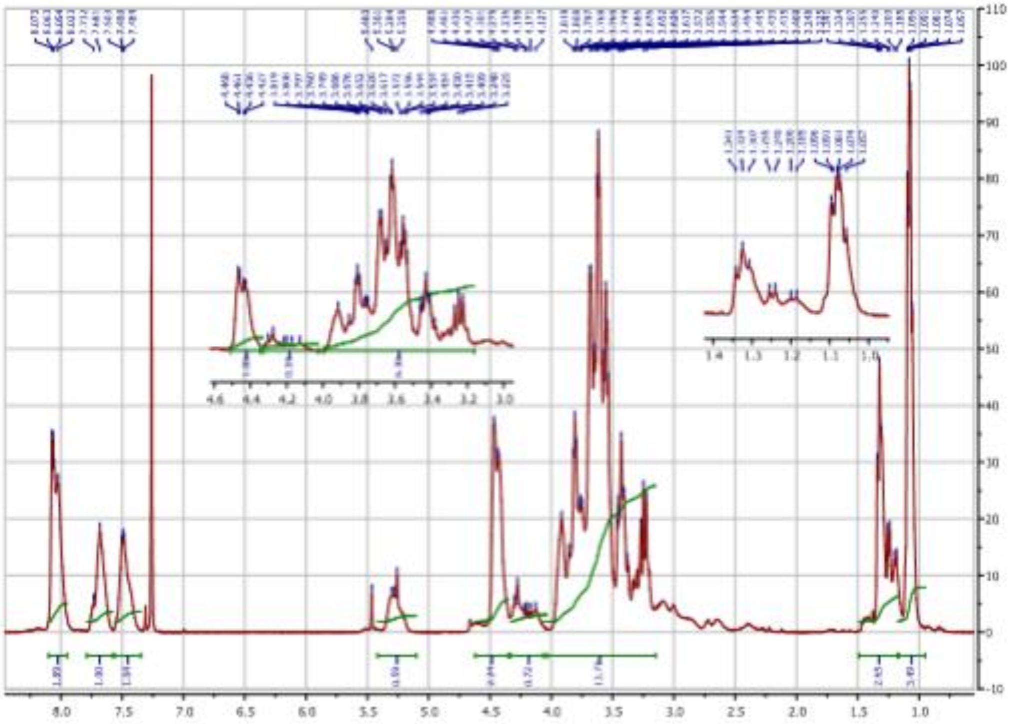
TA – terephthalic acid derived from PET; * * EG – ethylene glycol derived from PET; * * * PG – 1,2 propylene gycol moieties from PO (propylene oxide) (calculated by the enhanced weight of the reaction mass); 1 Karl Fischer; 2 Gas chromatography.

Analysis of the results indicates that the polyester-polyols, P1-P5 produced by the new series of chemical reactions have a lower acidity index relative to the PB produced by the conventional esterification process. This is a benefit over the conventional recycling process, as no detrimental influence on the foaming catalytic efficiency is created alongside the increased hydrolytic stability of polyester and polyols. A limiting parameter of polyurethane foam technology is related to the free glycol content that must be as limited as practicable. As can be seen in Table 1, all polyols have a comparable OH value of about 300 mg KOH / g in the range of standard polyols for rigid polyurethane foams (250-400 mg KOH / g). Polyols have low viscosity characteristics and are very good for the manufacturing of polyurethane (PU), with values up to 15000 cP approved. The P1 – P4 polyester-ether polyols are liquids, while the one produced by gluing the PET waste with isosorbide indicated a paste aggregation. A detailed study of the chemical structure and physico-chemical properties of the polyester etheric polyols obtained offers confirmation that the method produced is superior to the standard technique. In terms of economic efficiency, the suggested synthetic route requires a lower temperature, a shorter reaction period (3 h at 200o C for glycolysis, comparable to the classical method; 4-5 h at 120-140 oC for subsequent phases vs 6-8 h at 240-250 oC in the classical procedure) and no by-products. This is consistent with the findings set out above, which indicate that the use of propylene oxide generated polyols with a lower acidity index and a low free glycol content relative to standard methods (PB in Table 1).

H-NMR spectra of polyester-polyols

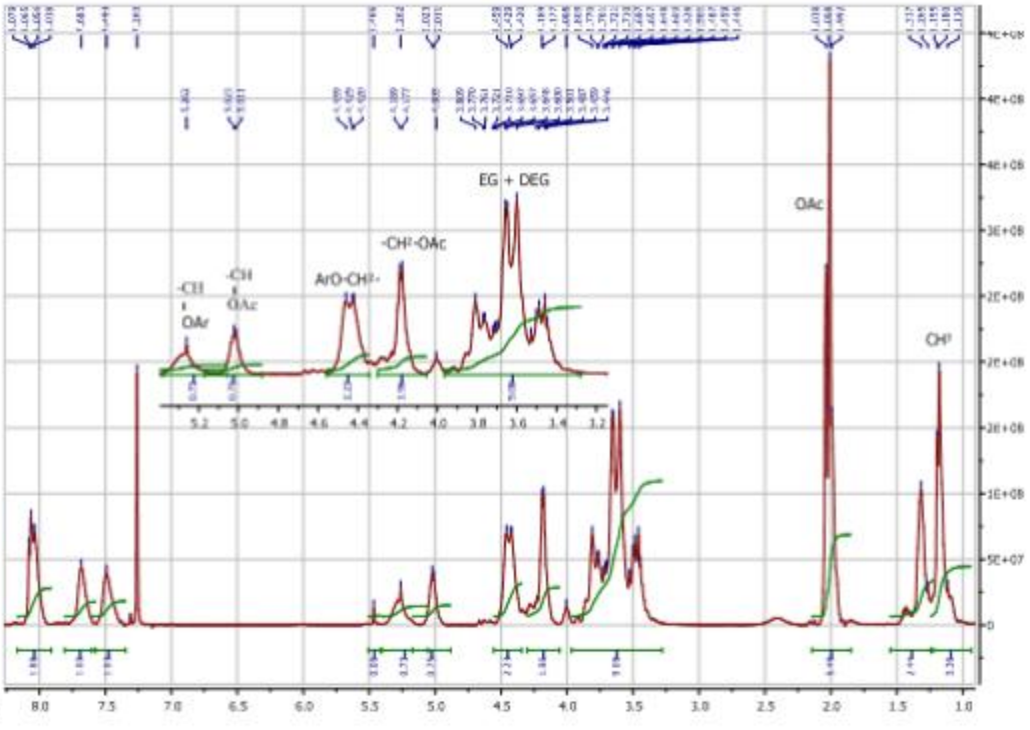
The chemical composition of the reaction products was calculated by 1 H-NMR spectroscopy in deutered chloroform. The 1 H-NMR range for the P2 polyester-ether polyol sample as seen in Figure 1, a. Detailed spectrum study indicates the development of both ester and ether group polymers. The continuum includes three characteristic chemical changes for aromatic protons in the 8.1 – 7.4 ppm range applied to the monoester and polyester-ether aromatic benzene groups. The most damaged signal was assigned to the terephthalic moiety, whereas the other two belonged to the phthalic systems. Upfield signals found from 1.3 – 1.0 ppm are allocated to the propylene glycol methyl protons and are detected as multiplets due to the tactical / isotactic position of these classes inside the dimer, trimer, etc. The range is very complex, but it can be differentiated between the aryl bound signals PG and DEG at 5.3 and 4.5 ppm, as well as the free glycol signal at 3.4 – 3.2 ppm, along with the ethylene glycol signals of glycolized PET. First, the multiplet at 4.4–4.2 ppm was allocated as ARO — CH2—CH(CH3)—OH to the main alcohol to bonded propylene glycol, while the 5.3–5.2 ppm multiplet was allocated to the secondary alcohol group of bonded propylene glycol, ARO — CH2—CH(CH3)—OH. The signature aryl-DEG signal is based about 4.5 ppm, whereas the ethylene glycol chemical change is measured at 4.6 ppm. The association of the convergence of the signals referring to the methyl groups of the PO moieties with that of the signals allocated to the aromatic protons of the phthalic units enables the calculation of the PO / PA ratio to be 3.8, which is compatible with the measured sum of the reacted PO.

The derivatization of the polyester-ether polyols obtained with acetic anhydride was done to increase the consistency and correct the errors. In this case (fig . 1, b) a better separation of proton chemical shifts has been observed which allows for an eloquent assignment of structural features. Acetyl protons (OAc) was detected at 2.0 ppm, whereas chemical changes at 5.4 – 4.1 ppm was due to PG and DEG functional ester (Fig . 1, b). The aromatic protons resonate in the predicted area , i.e. as three broad, de-shaped signals allocated as mentioned above. The multiplets related to the acetylated hydroxyl groups are now distinctly divided and present downfield adjustments for the aromatic bonded groups (fig.1,b for the chemical assignment). Through contrasting the signal of the aromatic protons to the acetyl-functionalized hydroxyl units, a content of 1,87 hydroxyl per aromatic unit can be inferred. Detailed study of the signal integrations enables the estimation of 25:75 per cent of the embedded propylene glycol in ester and ether bond. The primary / secondary hydroxyl group ratio was estimated to be 2.44 to 1 with a free propylene glycol value of 15% (mol) of the total PO moieties. For the P5 polyester-ether application, the 1 H-NMR range of the reaction product after monoesterification with phthalic anhydride accompanied by esterification / etherification with propylene oxide as shown in Figure 2 a when PET glycolysis was done with isosorbide. The multiplets of 8.0-7.5 ppm are representative of the benzene groups of the embedded phthalic units of the polyester-ether polymer. As though,



a)

Fig. 1. 1 H-NMR spectra of P2 polyester-ether polyol, as such



b)

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

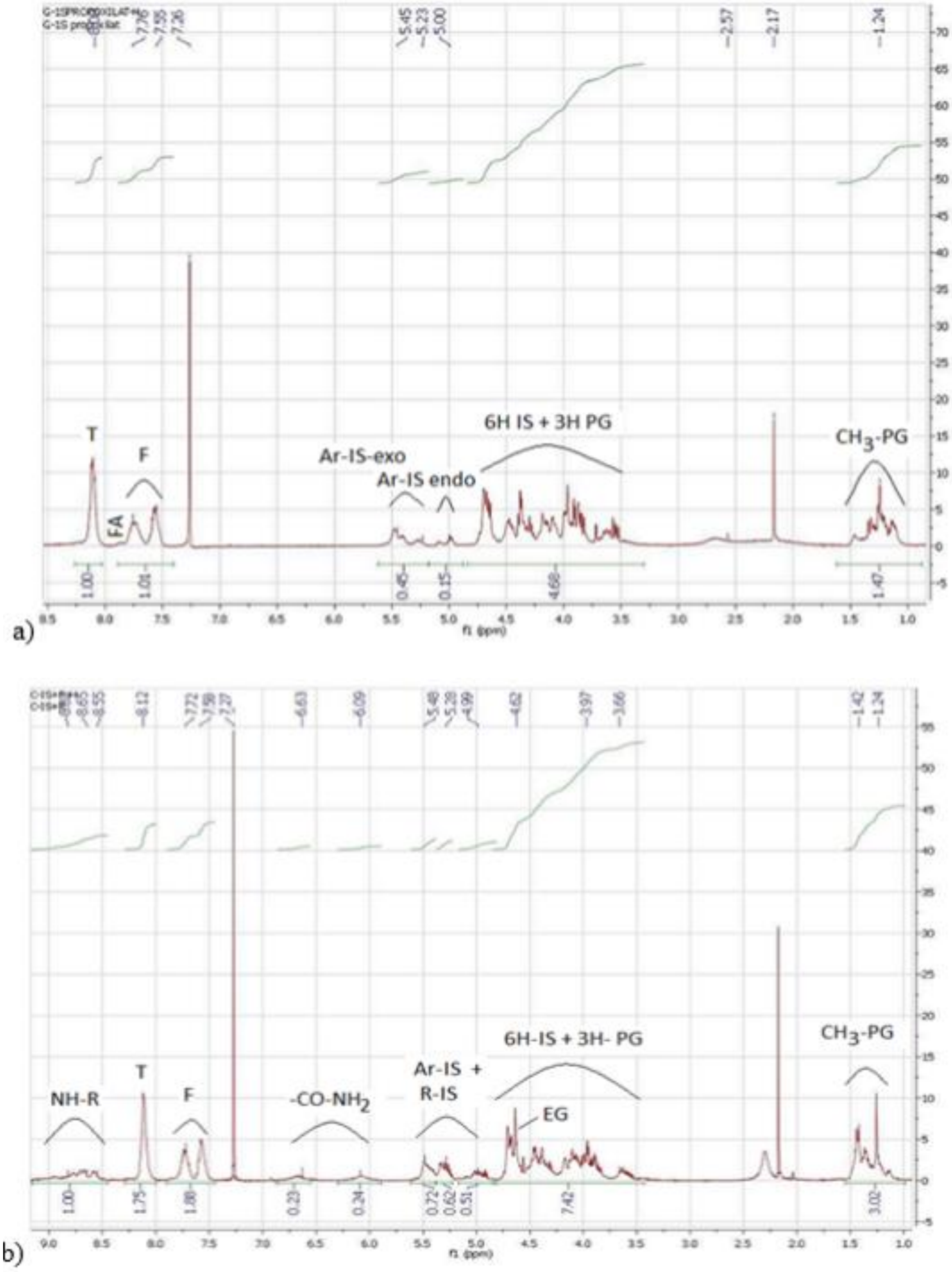
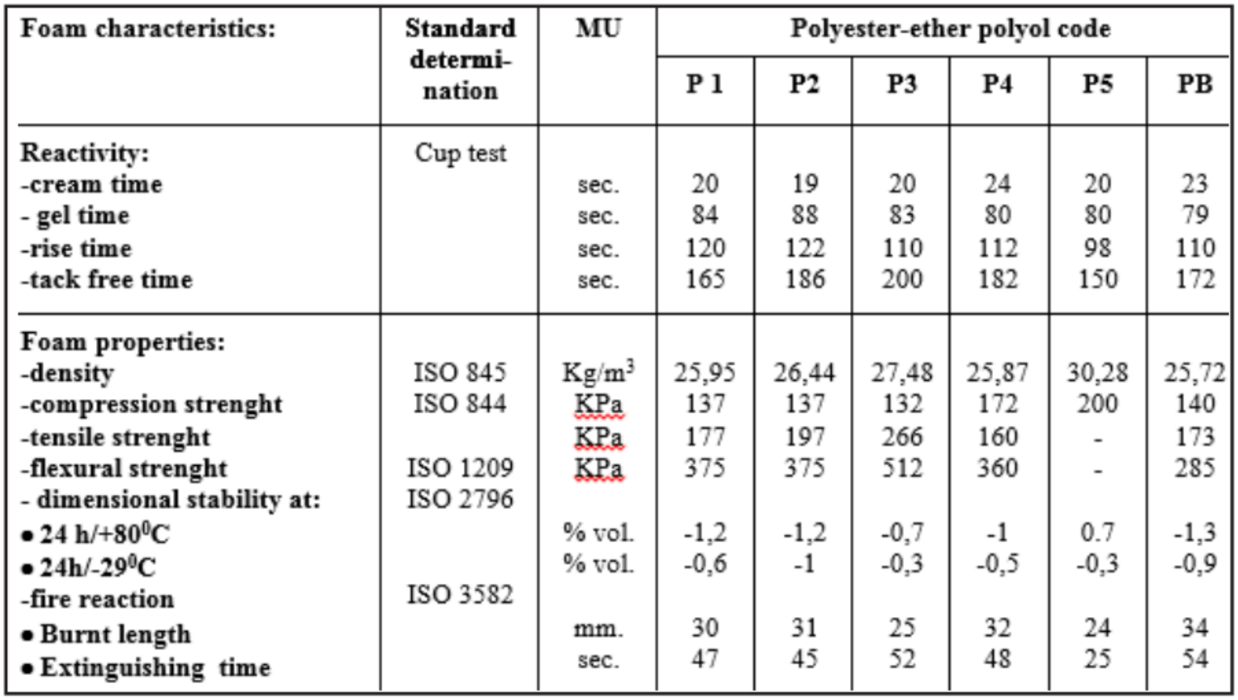


Fig. 2. 1 H-NMR spectra of experimental polyesterpolyol P5, as such (a) and derivatized with trichloroacetyl isocyanate Cl3 C–CO–N=C=O (b)

The methyl protons of the propylene glycol units were stated to be approximately 1.2 ppm. The association of the combination of the signals belonging to the methyl groups of the PO moieties with that of the signals allocated to the aromatic protons of the phthalic units enables the calculation of the PO / PA ratio to be 2.1. The assignment of the isosorbide and propylene glycol methyne protons is seen in Figure 2a. The endo-and exo-reacted hydroxyl groups of isosorbide diol are moved downfield amongst Fig. 1. 1 H-NMR spectra of P2 polyester-ether polyol, acetilated (b) 5.4 and 4.9 ppm as a result of their interaction with aromatic groups and in line with the literature[17,18]. The ratio of ester to ether embedded glycol is 47:53 per cent. Starting with terephthalic acid (noted T on the scale seen in fig. 2,a), assumed to be 1 mol, the corresponding integral per proton is equivalent to 0.25. Study of the exo / endo isosorbide proton integrals (0.3 in the spectrum) indicates that 1.2 moles of isosorbide are available as Ar-IS. Taking into consideration the volume of isosorbide required 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 Ar-IS generated by 1 H-NMR spectroscopy (1.2 mol), a conversion of 86 per cent was calculated for aromatic-bonded isosorbide fractions. As a consequence, the remaining 14 per cent could be in the form of free diol or eterified diol through self-reaction or PO. The understanding of the 1-H-NMR spectrum was verified by derivatizaton with trichloroacetyl isocyanate[19], a successful agent in the assignment of the resonance signal of the free OH groups (Fig . 2, b) This derivative reagent shapes the corresponding urethane when reacts with hydroxyl groups and amide, respectively, when water is present, with characteristic resonances for the first compounds and Free hydroxyl groups have been found to be 1.1 per aromatic band. The ratio of secondary OH groups to IS and PG per aromatic unit ratio observed to be 1.2 contributes to the result that free OH groups are predominantly all secondary. The presence of water in the solution mixture is indicated by the typical amide protons at 6.1 and 6.6 ppm. Detailed study of signal integrations makes the calculation of the ratio of free OH groups of isosorbide per OH groups of isosorbide esterified with aromatic units as being about 1.1.

Characteristics of the polyurethane rigid foams

Characterization outcomes of polyurethane foams are presented in Table 2. The structure-property of the polyols defines the efficiency of rigid polyurethane (PU) foams. The characteristics of PU foams are identified for P1 to P5 polyols and compared to PB-polyol produced through the traditional PET recycling method. Foam extracted from Example, DEG and DPG (P1 to P4) had a density of about 25 kg / m3, close to the standard value for rigid sandwich-panel foam formulation. A slight rise in density to 30 kg / m3 was found in the case of foam-containing isosorbide-based polyols. Preparation of foams also showed that all the polyester ether polyols tested are consistent with the traditional polyether polyols used for PUR foams, which together form stable and homogeneous mixtures. Physico-mechanical and flame retardant properties of the resulting rigid polyurethane foam up to 30% wt. The content of polyester-ether polyols was at least close to the properties of foam generated from PET waste by traditional recycling (PB) methods. Isosorbide-containing polyol contributes to increased compression strength, dimensional stability and fire reaction of the resulting PUR foam.

CONCLUSIONS

Polyester-ether polyols is prepared using a clean process consisting of PET waste glycolysis with typical diols (diethylene glycol and diethylene glycol / dipropylene glycol mixture), monoesterification of phthalic anhydride materials, accompanied by propoxylation under reasonably mild conditions. In addition, the procedure was performed against green chemistry by utilizing a non-toxic bio-proven diol, such as isosorbide, to cleave the PET strand. Polyester-ether polyols have been described by chemical processes, realistic viscosity tests, gas chromatography and 1 H-NMR spectroscopy. The results showed that liquid polyester-ether polyols with comfortable dynamic viscosities and low free glycol content were obtained when diethylene glycol and dipropylene glycol were used as cleaving reagents, while polyester-ether polyol developed by cleaving PET waste with isosorbide showed a paste aggregation and a low free low molecular weight glycol content. 1 The HNMR spectra offered details on the structure of the materials, allowing for the creation of chemical reactions hypotheses.

Experiments performed to test polyester ether polyols in the formulation of polyurethane rigid foams have shown that they are all compliant with popular polyether polyols for PUR foams, binding together robust and homogeneous mixtures. Physico-mechanical and flame retardant properties of received rigid polyurethane foams up to 30% wt. The polyol portion is better or at least close to the properties of foam generated from PET waste by traditional recycling methods. Polyol containing isosorbide has contributed to an increase in the physico-mechanical and flame retardant properties of PUR foam. The importance of this research work is provided by the fact that a clean technique has been developed for the synthesis of polyester ether polyols from PET waste, which is useful for the preparation of rigid polyurethane foams without the processing of by-products or waste.

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