

Research Article

Modification of the Rigid Polyurethane-Polyisocyanurate Foams

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Received 15 May 2013; Accepted 22 October 2013; Published 29 January 2014

Academic Editor: Cengiz Soykan

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The effect of polyethylene glycol 1500 on physicomaterial properties of rigid polyurethane-polyisocyanurate (PUR-PIR) foams has been studied. It was found that application of polyethylene glycol 1500 for synthesis of foams in amount from 0% to 20% *w/w* had an effect on reduction of brittleness and softening point, while the greater the increase in compressive strength the higher its content in foam composition was. Wastes from production of these foams were ground and subjected to glycolysis in diethylene glycol with the addition of ethanalamine and zinc stearate. Liquid brown products were obtained. Properties of the resulting products were defined in order to determine their suitability for synthesis of new foams. It was found that glycolysate 6 was the most suitable for reuse and its application in different amounts allowed us to prepare 4 new foams (nos. 25, 26, 27, and 28). Properties of foams prepared in this manner were determined and, on their basis, the suitability of glycolysates for production of rigid PUR-PIR foams was evaluated.

1. Introduction

The rigid polyurethane foams are polyadditive plastics characterized by the lowest thermal conductivity among all the materials applied as the heat insulators [1–3]. Their very good insulating properties are not fully used due to their high price. Therefore, the most often applied material for insulating the buildings and other objects is foamed polystyrene. The polyurethane foam of 5 cm in thickness gives the same insulating effect as the foamed polystyrene of about 10 cm. Reduction of foam price is possible by applying such fillers in foam composition, which do not cause deterioration of the foam functional properties. The fillers applied to prepare rigid polyurethane foams should fulfill many requirements. They should be easily dispersed in polyol premixes and should not worsen conditions of processing. A good filler should be characterized by as low sedimentation in suspension as it is possible and even in the case when some sediment is formed, it should be easily mixed. The fillers should not absorb the components of composition, especially catalysts, since the decrease in their concentration can result in disturbances in polyaddition process [4].

When the costs of PUR-PIR foam production will be reduced, these foams will become competitive to other materials applied for insulating, for example, foamed polystyrene, mineral wool, and others.

During manufacturing (foaming) and moulding of rigid polyurethane foams, the waste products are produced. Waste products usually consist of defective casts, leakage from the mould, and residues from cleaning of devices and moulds. Other groups are waste materials such as, for example, packages. Part of polyurethane foam waste can come from recycling of cars. Used wrappings of heat pipelines (heat insulations and postconsumer waste) and others are also a source of rigid polyurethane foam wastes. Method of waste combustion is noneconomical. Reduced-in-size foam wastes are also applied as fillers to produce new foams (mechanical recycling). These fillers have often unfavourable effect on physicomaterial properties of the foams obtained. For the obvious reasons, methods based on waste decomposition by the use of chemical reagents to obtain liquid products become more and more popular [5–11]. The new products can be successfully used to produce polyurethane plastics. In the early 1970s of last century in Poland, this method of recycling (utilization) was investigated by research team of

Department of Organic Technology in University of Technology and Agriculture in Bydgoszcz under the direction of Associate Professor Kozłowski and others [12]. The method of utilization consists in decomposition of waste polyurethane (PUR) and polyurethane-polyisocyanurate (PUR-PIR) foams in ethylene glycol in presence of catalysts at temperature from 150°C to 250°C for 2 to 10 hours.

Application of polyurethane foams as insulating materials is significantly limited by their thermal and heat resistance [13–18].

Heat resistance is connected with the physical changes occurring in insulation or foam product under the influence of temperature and the forces imposed. It is defined by the softening point and the method of determination. The molecular weight of plastic remains unchanged during these changes.

Thermal resistance is relevant to the breakdown temperature of the weakest bonds in foams and it is accompanied by the degradation of polymer. Molecular weight of foam is reduced. The softening point of the polyurethane foams is by tens degrees lower than the temperature of their decomposition.

Thermal resistance of foams is connected mainly with temperature of the thermal dissociation of bonds occurring in foams. The basic bond is urethane bond, which is more often formed in reaction between aromatic polyisocyanate and aliphatic polyol. Its temperature of thermal dissociation is about 200°C. Ester and ether bonds (characterized by temperature of dissociation of about 260°C and 350°C, resp.) are introduced into polymer chain with polyol. Polyols are oligomerols formed by polyoxyalkylation of the low molecular weight compounds. Polyoxypropylene fragments occurring in polyurethanes decompose at temperature within the range from 210°C to 230°C. Besides polyurethane bonds, small amounts of allophanate bonds appear and their temperature of dissociation is 106°C.

Water applied in order to obtain CO₂ (porophor) reacts with polyisocyanate which results in formation of urea and biuret bonds whose temperatures of dissociation are 250°C and from 130°C to 145°C, respectively [3].

Isocyanurate and carbodiimide bonds (temperatures of dissociation about 300°C and 240°C, resp.) were introduced into the chain of the macromolecular compound as a result of polyisocyanate excess in relation to polyol (Table 1).

The aims of studies were as follows: (1) the determination of the effect of polyethylene glycol 1500 additive on physico-mechanical properties and thermal resistance of block rigid polyurethane-polyisocyanurate foams, (2) performance of foam chemical recycling by alcoholysis combined with aminolysis, (3) preparation of the new materials by applying liquid products of decomposition of the previously synthesized PUR-PIR foams (initial foams), and (4) comparison of physico-mechanical and thermal properties of the initial foams and the new foams prepared with addition of products of their decomposition (recyclates).

2. Experimental

2.1. Materials. The polyether with trade name Rokopol RF-55 (product of oxypropylation of sorbitol $L_{OH} = 495$ mg

TABLE 1: Temperatures of cleavage of chemical bonds occurring in PUR-PIR foams.

No.	Bond	Temperature of cleavage (°C)
1	Urethane	200.0
2	Ester	260.0
3	Ether	350.0
4	Allophanate	106.0
5	Urea	250.0
6	Biuret	140.0
7	Carbodiimide	240.0
8	Isocyanurate	300.0

KOH/g, produced by NZPO “Rokita,” Brzeg Dolny, Poland) and Casmonate 200 PMDI (technical polyisocyanate whose main component is diphenylmethane 4,4'-diisocyanate, made in Japan) were used to prepare the rigid PUR-PIR foams. Density of Cosmonate 200PMDI at temperature of 25°C was 1.04 g/cm³ and its viscosity was approximately 1300 mPa·s. Content of NCO groups was 31%. Polyether, products of foam glycolysis (recyclates) and polyisocyanate were characterized according to the following standards: ASTM D 2849-69 and ASTM D 1638-70.

Anhydrous potassium acetate in the form of 33% solution in diethylene glycol (Catalyst-12, POCh Gliwice, Poland) and DABCO (triethylenediamine produced by Hüls, Germany) in the form of 33% solution in dipropylene glycol were applied as catalysts in the foam composition. The polysiloxypolyalkyleneoxydimethylene surface-active agent Silicone L-6900 (Witco Corp., Sweden) was used as a stabilizer of the foam structure. Foams were obtained in the presence of polyethylene glycol 1500 (white solid, dissolved in water, KOCH_LIGHT LABORATORIES LTD, Colnbrook, Buks, England). This glycol is a mixture of polymers with general formula H-(OCH₂-CH)_n-OH corresponding to mean relative molecular weight of about 1500.

2.1.1. Determination of Recipes for Rigid PUR-PIR Foams Preparation. The basis for the determination of recipes for preparation of the rigid PUR-PIR foams was the values of hydroxyl number of Rokpol RF-55 and products of glycolysis. They were developed taking into account also the percentage of isocyanate groups in PMDI applied. The basic raw materials (isocyanate and polyol) and products of glycolysis are chemically impure compounds. Therefore, recipes for synthesis of rigid foams were prepared taking advantage of gram-equivalents calculated by the following formulas:

$$R_{OH} = \frac{56100}{L_{OH}}, \quad (1)$$

where R_{OH} is hydroxyl gram-equivalent and L_{OH} is hydroxyl number (determined by titration):

$$R_{NCO} = \frac{4200}{\% NCO}, \quad (2)$$

TABLE 2: Receipts used to prepare rigid PUR-PIR foams with addition of polyethylene glycol 1500 (initial foams).

Raw material, g	Number of foam								
	0	1	2	3	4	5	6	7	8
Rokpol RF-55	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
Polyethylene glycol 1500	00.0	8.6	17.2	25.8	34.4	43.0	51.6	60.2	68.8
Silicone L 6900	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6
DABCO	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8
Catalyst 12	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5
Antiblaze TMCP	34.6	34.6	34.6	34.6	34.6	34.6	34.6	34.6	34.6
Water	3.15	3.15	3.15	3.15	3.15	3.15	3.15	3.15	3.15
Ongromat 30–20	265.7	284.0	284.0	284.0	284.0	284.0	284.0	284.0	284.0

* 2.5% (8.6 g), 5.0% (17.2 g), 7.5% (25.8 g), 10.0% (34.4 g), 12.5% (43.0 g), 15.0% (51.6 g), 17.5% (60.2 g), and 20.0% (68.8 g) w/w of polyethylene glycol were added with respect to the sum of Rokpolu RF-55 and Cosmonate 200 PMDI weight.

TABLE 3: Basic utility properties of rigid PUR-PIR foams (numbers of foams as in Table 1)

No. of foam	Apparent density kg/m ³	Compressive strength kPa	Brittleness %	Softening point °C	Oxygen index %	Retention %	Loss of volume %	Loss of mass %
0	36.9	221.7	41.1	230.0	22.1	76.6	0.00	0.00
1	29.4	229.3	38.3	226.6	22.5	77.7	-0.5	0.2
2	29.2	236.2	36.6	223.6	22.4	79.9	-0.8	0.5
3	29.6	239.3	30.1	221.9	22.2	82.7	-1.2	0.5
4	29.8	242.1	28.7	219.7	21.8	84.4	-1.0	0.4
5	29.7	247.7	25.3	212.1	21.5	85.9	-1.1	0.6
6	29.7	250.1	22.4	209.4	22.5	87.2	-0.9	0.4
7	29.6	257.2	22.0	206.1	23.2	88.3	-0.9	0.5
8	29.5	265.9	21.7	205.9	23.4	88.8	-0.8	0.5

where R_{NCO} is isocyanate gram-equivalent and % NCO is percentage of isocyanate groups (determined by titration).

Amount of isocyanate was calculated taking into account constant initial ratio of NCO:OH groups equal to 3:1. The calculated amount was increased by the weight of isocyanate indispensable for reaction with water resulting in liberation of porophor-gaseous CO₂.

Then, the contents of auxiliaries, which generally do not contain hydroxyl and isocyanate groups, were determined. Content of catalysts, flame retardants, and surfactants were expressed in % w/w per 100% w/w of the total amount of polyols and polyisocyanate. The calculated amounts of all the above mentioned components were mixed together and they constituted polyol premix, which then was mixed with isocyanate to obtain foams.

2.2. Method of Preparation of Rigid PUR-PIR Foams. The foams were prepared in laboratory scale by one-stage method, according to Table 2 (with polyethylene glycol 1500) and Table 5 (with products of glycolysis), from two-component system at the equivalent proportion of NCO to OH groups equal to 3:1. Component A was obtained by precise mixing (speed of stirrer—1800 rpm and time—15 sec) of the respective amounts of Rokpol RF-55, catalysts, flame retardant, surface-active agent polyethylene glycol 1500, and recyclates. Component B was Cosmonate 200 PMDI. Both components (A and B) were mixed (1800 rpm, 10 sec) at respective weight

ratios and poured into a metal rectangular tray where they were foamed in time dependent manner on the composition. An open mould was applied in our studies in order to enable the so-called free expansion of foam. The open mould was made from steel (thickness of 3 mm and internal dimensions 25 × 25 × 25 cm). Five foaming operations were conducted for each system. During synthesis, the course of foaming of the reaction mixture was monitored by measuring the respective technological times (always measured from the moment when all components were mixed), that is, start time (reaching the so-called “creamy state,” that is, beginning of foam expansion), time of expansion (to the moment when the foam attained maximum volume), and total time of gelation (to the moment when free surface of foam ceased to stick to a clean glass rod). The expanded foams were removed from the mould and thermostated for 4 hours at temperature of 120°C. Then, foams were cut to samples according to the obligatory standards and their physicomechanical properties were determined. Band-saw was applied for cutting.

2.3. Determination of the Foam Properties. Physicomechanical properties of the obtained PUR-PIR foams were determined according to standards accepted for rigid polyurethane foams.

2.3.1. Determination of Apparent Density. Apparent density was determined according to ISO 845-1988 standard; tests

TABLE 4: Properties of the liquid products of the initial foam decomposition.

No. of foam	Content of polyethylene glycol 1500 [%]	Density (temp. of 25°C) [kg/m ³]	Viscosity (temp. of 25°C) [mPa·s]	Hydroxyl number [mg KOH/g]
0	0.0	1100.0	2410.0	420.0
1	2.5	1130.0	2425.0	433.0
2	5.0	1150.0	1965.0	437.0
3	7.5	1170.0	1981.0	444.0
4	10.0	1110.0	3325.0	450.0
5	12.5	1126.0	3337.0	457.0
6	15.0	1095.0	3977.0	461.0
7	17.5	1134.0	4011.0	477.0
8	20.0	1145.0	4237.0	481.0

were carried out for 3 samples of each foam in the form of rectangular cubes (volume of 125 cm³). Samples of foams were measured by a slide caliper with an accuracy of 0.1 mm and were weighted accurately to 0.0001 g. Arithmetic mean from densities calculated as the mass to volume ratio was accepted as the result.

2.3.2. Determination of Compressive Strength at Sample Deformation of 10%. Compressive strength was determined according to ISO standard 844:1993. Tests were carried out on 5 foam samples (dimensions 50×50×50 mm). The maximum load causing reduction in height of foam sample by 10% with respect to the initial one in direction of foam expansion was determined. The compressive strength at deformation by 10% was calculated as a ratio of load causing deformation by 10% to the initial surface of sample cross-section. The mean value from 5 measurements was accepted as the result.

2.3.3. Determination of Brittleness. The determinations were carried out according to ASTM C-421-61 standard in a cubical box (190 × 197 × 197 mm) made from an oaken wood and rotating about the axis with a speed of 60 ± 2 rpm. The box was filled with 24 oak cubes of side 20 mm. Brittleness was calculated as a loss in mass (in percent) of 12 foam cubes (side of 25 mm) during drum rotation for 10 minutes in relation to their initial mass. Consider

$$K = \frac{m_1 - m_2}{m_1} 100\%, \quad (3)$$

where K is brittleness in %, m_1 is sample mass before test, and m_2 is sample mass after test.

Determination of the foam flammability was done according to simplified chimney test (ASTM D 1692-59T).

Three samples of foams with dimensions of 150 × 20 × 20 mm were subjected to test. Combustion was performed in a vertical column (chimney) of 300 × 57 × 54 mm by a flame from gas burner supplied with propane-butane. The weighted sample was brought into contact with burner flame for 10 seconds and then, the burner was removed and time of the sample free burning was measured by stopwatch. After combustion, the samples were weighted once again. The results were time of free burning and retention in chimney

test. Residue of mass (retention) after combustion (in %) was calculated from the formula:

$$R = m_2 m_1^{-1} \times 100\%, \quad (4)$$

where R is retention (residue after combustion) in %, m_1 is mass of sample before burning [g], and m_2 is mass of sample after burning [g].

2.3.4. Determination of Flammability according to Horizontal Test. Tests were performed for 3 foam samples of dimensions 150 × 50 × 13 mm according to ASTM D-1692-74 standard. The tested samples in horizontal position with marked line at a distance of 125 mm were burned by the flame from propane-butane burner for 60 seconds. Then, the burner was removed and time of the sample free burning was measured by stopwatch. The range of flame propagation in mm and time of free burning in horizontal test were accepted as results.

2.3.5. Determination of Changes in Linear Dimensions and Volume (ISO 1923:1981). The determinations were performed for 3 samples (dimensions 50 × 50 × 50) of each foam with indicated direction of growth. Changes in the linear dimensions and volume were determined after 48 hours of sample thermostating at temperature of 120°C. Change in linear dimensions was determined in accordance with direction of the foam growth and it was calculated in % from equation

$$\Delta l = \frac{l - l_0}{l_0} \times 100, \quad (5)$$

where l_0 is length of sample before thermostating and l is length of sample after thermostating.

However, change in volume (in %) was calculated according to formula:

$$\Delta V = \frac{V - V_0}{V_0} \times 100, \quad (6)$$

where V_0 is volume of sample before thermostating and V is volume of sample after thermostating.

Dimensions were measured by a slide caliper with accuracy to 0.1 mm. Samples were thermostated in a drier with circulation of air.

TABLE 5: Receipts of foams containing recyclates of standard foam (foams 1–4) and polyethylene glycol 1500 (foams 5–36).

No. of foam as in Table 1	No. of foam obtained from recyclates	Rokpol RF-55 (g)	Products of foam decomposition (g)										
			0	1	2	3	4	5	6	7	8		
	0.0	56.7	0.0										
0	1	51.0	6.7										
	2	45.3	13.4										
	3	39.6	20.0										
	4	34.0	26.7										
1	5	51.0		6.5									
	6	45.3		13.0									
	7	39.6		19.4									
	8	34.0		25.9									
2	9	51.0			6.4								
	10	45.3			12.8								
	11	39.6			19.3								
	12	34.0			25.7								
3	13	51.0				6.3							
	14	45.3				12.6							
	15	39.6				19.0							
	16	34.0				25.3							
4	17	51.0					6.2						
	18	45.3					12.5						
	19	39.6					18.7						
	20	34.0					25.0						
5	21	51.0						6.1					
	22	45.3						12.3					
	23	39.6						18.4					
	24	34.0						25.5					
6	25	51.0							6.1				
	26	45.3							12.2				
	27	39.6							18.2				
	28	34.0							24.3				
7	29	51.0								5.9			
	30	45.3								11.8			
	31	39.6								17.6			
	32	34.0								23.5			
8	33	51.0										5.8	
	34	45.3										11.7	
	35	39.6										17.5	
	36	34.0										23.3	

2.3.6. *Determination of Loss in Mass (PN-ISO 4590:1994).* The loss in mass was determined for 3 samples (50 × 50 × 50 mm) after 48 hours of thermostating at temperature of 120°C in drier with circulation of air. Samples were weighted before and after thermostating. Loss in mass was calculated in percent from the formula:

$$\Delta m = \frac{m_0 - m}{m_0}, \quad (7)$$

where m_0 is mass of sample before thermostating and m is mass of sample after thermostating.

2.3.7. *Determination of Softening Point.* Softening point was determined as a thermal resistance under compressive stress according to DIN 53 424 standard. Samples of foam (20 × 20 × 20 mm) were subjected to the action of compressive load of 0.25 kG/cm² longwise a direction of the foam expansion.

TABLE 6: Basic utility properties of rigid PUR-PIR foams with addition of glycolysis products (nos. as in Table 4).

No. of foam	Apparent density kg/m ³	Compressive strength kPa	Brittleness %	Softening point °C	Oxygen index %	Retention %	Change of volume %	Loss of mass %
0	36.9	221.7	41.1	230.0	22.1	76.6	0.0	0.0
1	35.5	222.1	40.3	229.8	22.1	76.6	0.0	0.0
2	35.4	222.5	38.2	229.3	22.5	77.8	0.0	0.0
3	35.9	223.1	36.7	229.1	22.7	77.9	0.0	0.0
4	35.4	223.3	34.9	228.9	22.9	78.1	0.0	0.0
5	36.3	224.7	38.2	227.3	22.4	77.9	0.0	0.0
6	37.0	227.3	37.3	227.1	22.6	78.7	0.0	0.0
7	36.7	229.1	36.4	226.7	22.7	79.9	0.0	0.0
8	36.8	230.0	36.0	226.1	22.9	80.0	0.0	0.3
9	36.9	225.3	36.3	225.4	22.6	78.3	0.0	0.0
10	37.1	227.1	35.1	224.9	22.8	79.5	0.0	0.0
11	37.0	228.2	34.7	223.7	23.0	80.3	0.0	0.0
12	36.9	228.9	34.1	223.3	23.0	81.3	0.0	0.0
13	37.5	226.3	33.7	223.5	22.8	79.4	0.0	0.0
14	37.7	227.7	32.5	221.1	23.0	80.2	0.0	0.0
15	37.8	228.5	31.3	219.7	23.1	81.7	0.0	0.2
16	37.9	229.3	30.1	218.9	23.1	81.6	0.0	0.0
17	38.9	231.2	30.1	220.7	22.8	79.6	0.0	0.0
18	36.6	236.3	28.3	218.6	23.0	80.9	0.0	0.3
19	38.7	239.7	26.4	217.7	23.2	81.7	0.0	0.1
20	38.8	240.2	23.0	216.4	23.5	82.9	0.0	0.0
21	37.7	233.3	27.1	218.9	22.9	80.0	-0.3	0.0
22	37.8	235.7	25.9	217.1	23.1	81.4	-0.5	0.3
23	37.9	237.8	23.0	215.9	23.6	82.7	-0.4	0.1
24	38.3	241.4	22.1	214.1	23.9	83.6	-0.6	0.1
25	38.7	240.1	25.1	227.7	23.7	82.9	0.0	0.0
26	38.9	244.7	23.4	227.1	23.9	83.9	0.0	0.0
27	38.9	246.4	21.1	224.7	24.5	84.8	0.0	0.0
28	39.4	249.9	18.4	224.1	25.1	86.4	0.0	0.0
29	37.7	237.4	27.1	218.7	22.7	79.9	0.0	0.2
30	37.9	238.9	25.4	216.5	22.9	80.3	0.7	0.6
31	37.9	242.7	23.2	213.9	23.0	80.8	0.9	0.7
32	38.1	243.8	20.7	211.9	23.9	81.7	0.3	0.7
33	37.1	234.4	30.1	215.5	23.0	81.0	0.0	0.0
34	37.3	236.1	28.4	213.7	23.6	82.6	0.0	0.0
35	37.1	237.9	26.2	211.3	23.9	83.4	0.7	0.6
36	37.7	238.6	23.3	209.7	24.7	84.7	0.9	1.1

Temperature rise during the test was 50° per hour. Temperature at which the sample was compressed by 2 mm was accepted as the softening point.

2.3.8. *Determination of Thermal Resistance.* The foams were grinded in Janetzky's ball mill and then, they were subjected to thermogravimetric analysis within the range of temperature from 20°C to 800°C. Thermal resistance of foams was determined under dynamic conditions in air atmosphere at

the heating rate of 5 deg/min. Tests were carried out using derivatograph produced by MOM Budapest (Paulik-Paulik-Erdey).

2.3.9. *IR Analysis.* IR analysis of rigid PUR-PIR foams was conducted by KBr technique within the range from 4000 cm⁻¹ to 400 cm⁻¹ by the use of Victor spectrophotometer (Brucker).

2.3.10. Content of Closed Cells. Content of the closed cells was determined in accordance to PN-ISO 4590:1994 standard by method II (dimensions of samples: 100 × 30 × 30 mm). This method is used for determining the percentage of closed cells in rigid porous plastics. It consists in the determination of the relative pressure drop (earlier calibrated for the volume standards) from the differences in indications on the scale of manometer whose one arm was opened to atmosphere.

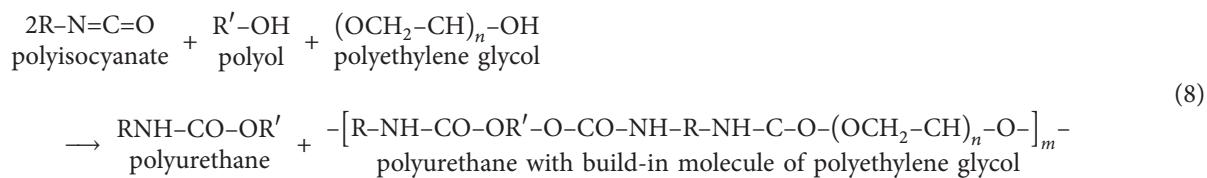
2.3.11. Heat Conductivity. Heat conductivity (value of the thermal conductance λ) of the foam samples (dimensions of 200 × 200 × 25 mm) was determined by the use of apparatus FOX 200 (Lasercomp). It allowed us to determine λ value within the range from 20 to 100 mW/(m·K). The method consists in determining the amount of heat flowing through a given material on opposite sides of sample in the time unit during steady heat flow at constant difference of temperature.

2.3.12. Decomposition of Rigid PUR-PIR Foams and Characteristics of Alcoholysis Products. Decomposition (glycolysis) of 9 types of rigid PUR-PIR foams (standard foam without filler), prepared from components presented in Table 2 (foams numbers 0–8), was performed in three-neck glass flask (0.5 dm³) equipped with a stirrer, reflux, and thermometer. Diethylene glycol (160 g, product POCH, Gliwice), ethanoloamine (40 g, product POCh, Gliwice), and catalyst – zinc stearate (3 g, product POCH Gliwice) were introduced into a flask. Content of the flask was heated in electric bath

to the mixture boiling point and then, 90.0 g (in portions of 15 g) of the grinded foam samples was dosed (laboratory screw-disk and ball mills). Alcoholysis was carried out at different temperatures (in the range from 150°C to 250°C). The reaction time ranged from 3.5 to 4.0 h. After completion of foam dosing, the reaction mixture was heated for another 2 hours at temperature from 200°C to 215°C in order to obtain homogeneous solution. The quantitative composition of degradation products was monitored during decomposition process. The following parameters were determined for the obtained products: density (PN-92/C-04504), viscosity (PN-86/C-89082.04), and hydroxyl number (PN-93/C-89052.03).

3. Results and Discussion

Rigid polyurethane-polyisocyanurate foams with polyethylene glycol 1500 were prepared by one-stage method in the proportion of isocyanate to hydroxyl groups 3:1. Blowing agent for the systems was carbon dioxide formed in reaction of PMDI with water. Addition of polyethylene glycol 1500 for synthesis of foams caused a slight extension of start, expansion, and gelation, times compared to standard foam, that is, from 14.1 s, 21.0 s, and 38.5 s (standard foam) to 15.1 s, 23.0 s, and 41.7 s (foams with 20% w/w of glycol), respectively. Thus, addition of polyethylene glycol 1500 results in lower reactivity of the mixture: Rokpol RF 55 and polyethylene glycol 1500 in relation to PMDI then commonly used polyol. Polyethylene glycol can be treated as a typical chain extension. Probable course of the reaction between isocyanate, polyol, and polyethylene glycol can be summarized as follows:



On the basis of IR spectrum, it was found that the prepared foams were characterized by the expected chemical structure of polyurethane-polyisocyanurate foams, since vibration spectra corresponding to both urethane bond (2180–1710 cm⁻¹) and isocyanurate ring (1710–1680 or 1410 cm⁻¹) occurred in their spectra.

Properties of polyurethane-polyisocyanurate foams (standard and with polyethylene glycol) are presented in Table 3. Apparent densities of foams containing polyethylene glycol 1500 were lower than that of standard foam (36.96 kg/m³). Apparent density of foams containing polyethylene glycol from 2.5% to 20.0% w/w was 29.5 ± 3 kg/m³. Polyethylene glycol probably behaves like a typical cross-linking compound facilitating formation of a more orderly structure of foams. Therefore, its presence in the foam causes a significant reduction in brittleness from 41.1% (standard foam without polyethylene glycol 1500) to 21.7% (foam no. 8).

The compressive strength increases as the content of polyethylene glycol 1500 is increased in foam composition. The limiting values are as follows: 221.7 kPa (foam no. 0) and 265.9 kPa (foam no. 8) and corresponding relationship is rectilinear.

Moreover, content of closed cells was determined in samples of foams. Their content increased in comparison with standard foam and was equal to 82.7% for standard foam, 83.6% for foam no. 1, and 90.3% for foam no. 8. Addition of polyethylene glycol 1500 causes decrease in water absorptivity. Absorptivity of water for standard foam was 6.3% v/v and it decreased to 3.7% v/v as the amount of polyethylene glycol was increased. It can be due to smaller share of closed cells in standard foam than in foams with addition of polyethylene glycol 1500.

Studies on loss of volume, loss of weight, and stability of linear dimensions after 48 h of thermostating at temperature of 120°C showed no effect of presence and content of

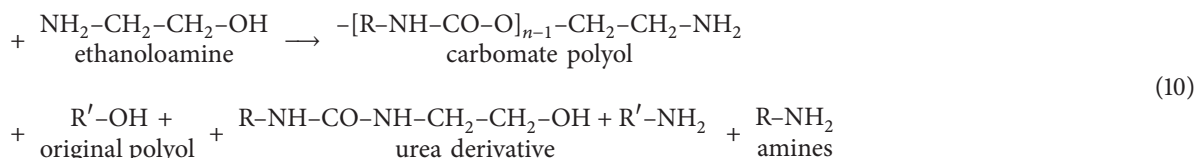
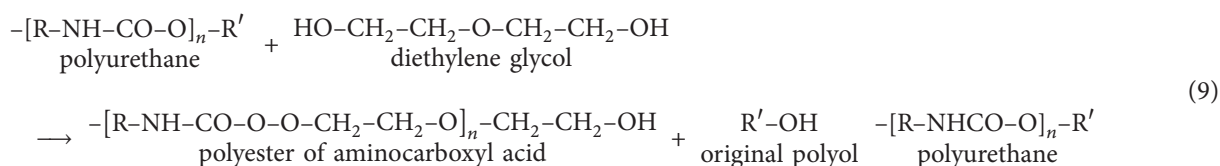
polyethylene glycol on changes in above mentioned properties.

As the content of polyethylene glycol was increased in foam composition from 0% to 20% *w/w*, flammability of foams slightly decreased resulting in a slight increase in oxygen index from 22.1% (foam number 0) to 23.4% (foam number 8) and retention from 76.6% (foam number 0) to 88.8% (foam number 8), respectively.

Thermal resistance of foams was characterized by thermogravimetric analysis in the previously described conditions. Example of thermogram of foam sample is presented in Figure 1. On the basis of TG (change of mass) and DTG (derivative of change of mass) curves, the characteristics were determined as follows [6–10]: temperature of the first loss of foam mass (T_1 , °C), extrapolated temperature of the beginning of the first loss of mass (T_2 , °C), temperature of the beginning of rapid decomposition of foam (T_3 , °C determined according to ISO 7111 standard as an intersection of tangents), and temperature of the highest rate of loss of foam mass (T_{max} , °C, corresponding to extreme on DTG curve). Thermogram showing dependence between temperatures T_1 , T_2 , T_3 , and T_4 and content of polyethylene glycol in foams is presented in Figure 2. As the content of glycol was increased from 0% to 20% *w/w*, T_1 , T_2 , T_3 , and T_4 increased from 85°C (foam 0, standard) to 104°C (foam 8), from 210°C (foam 0) to 223°C (foam 8), from 240°C (foam 0) to 258°C (foam 8), and from 280°C (foam 0) to 299°C (foam 8), respectively. The

cause of the first loss of mass is diffusion of carbon dioxide which acts as a blowing agent. It is formed in reaction of the excess of isocyanate groups with water. At temperature from 85°C to 104°C, diffusion of triethylenediamine (DABCO) from foams can occur. DABCO in the form of 33% solution in dipropylene glycol is applied as a catalyst for synthesis of PUR. Decomposition of urea formed by reaction of polyisocyanate with water and urethane groups has an effect on T_3 values. As the content of polyethylene glycol increases in foam composition, increase in participation of flexible segments occurs, among others, which affects increase in resistance to higher temperature. It results in increase of T_4 by 19°C.

Properties of the liquid products of decomposition of the initial foams [standard (foam 0) and with addition of 2.5% to 20% *w/w* (foams 0–8)] are presented in Table 4. As a result of foam glycolysis coupled with aminolysis, homogeneous liquid products of high viscosity (from 1100,0 mPa · s to 1170,0 mPa · s) and dark colour were obtained. Probably, they are a mixture of polyol applied for synthesis, urethane polyol, carbamates, and dicarbamates with terminal groups OH and NH₂. Increased temperature causes that also diamines, amines, and carbon dioxide are formed during reaction. Then, diamines react with urethane groups forming urea (aminolysis). In reaction of urethane groups with ethanoloamine, polyols were obtained as follows: urethane and original and urea derivatives (reactions (9), (10)):



The determined hydroxyl number of these products of decomposition is from 420.0 mg KOH/g to 481.0 mg KOH/g. The hydroxyl number was used to prepare recipes for the preparation of new rigid foams with their participation. The recipes of these foams are presented in Table 5 and their properties in Table 6. In addition to polyol and recyclates (products of glycolysis of foams) presented in Table 5, other components were introduced into foam composition in the following amounts: Silicone L-6900—5.16 g; DABCO 33-LV 3.1 g; catalyst 12—7.2 g; Antiblaze—51.6 g, distilled water—3.78 g; Casmonate 200 PMDI—286 g.

Addition of decomposition products (glycolysis) to foams in amount from 0.1 to 0.4 of chemical equivalent at simultaneous the same reduction of Rokpol 55 content in foams does not cause significant changes in parameters of processing and apparent density of the foams obtained. Start time of these

foams was from 17 s to 23 s, time of expansion and time of gelation did not exceed 57 s, and apparent density was within the range from 35.4 kg/m³ to 38.9 kg/m³ (Table 6).

Increase of recycle content in the new rigid foams from 0.1 to 0.4 of chemical equivalent causes the highest increase of compressive strength in case of addition of recycle obtained as a result of glycolysis of foams with addition of 15% *w/w* of polyethylene glycol, that is, from 221.7 kPa (foam 0) to 249.9 kPa (foam 28, with addition of 0.4 of chemical equivalent of foam glycolysis product with 15% of polyethylene glycol 1500). It was found that product of decomposition obtained from foam without fillers had insignificant effect on this property (foams 0–4, Table 5).

In all cases, brittleness was reduced with the increase of the content of glycolysis products in foam composition. Foams with addition of 0.4 of chemical equivalent (foams 28)

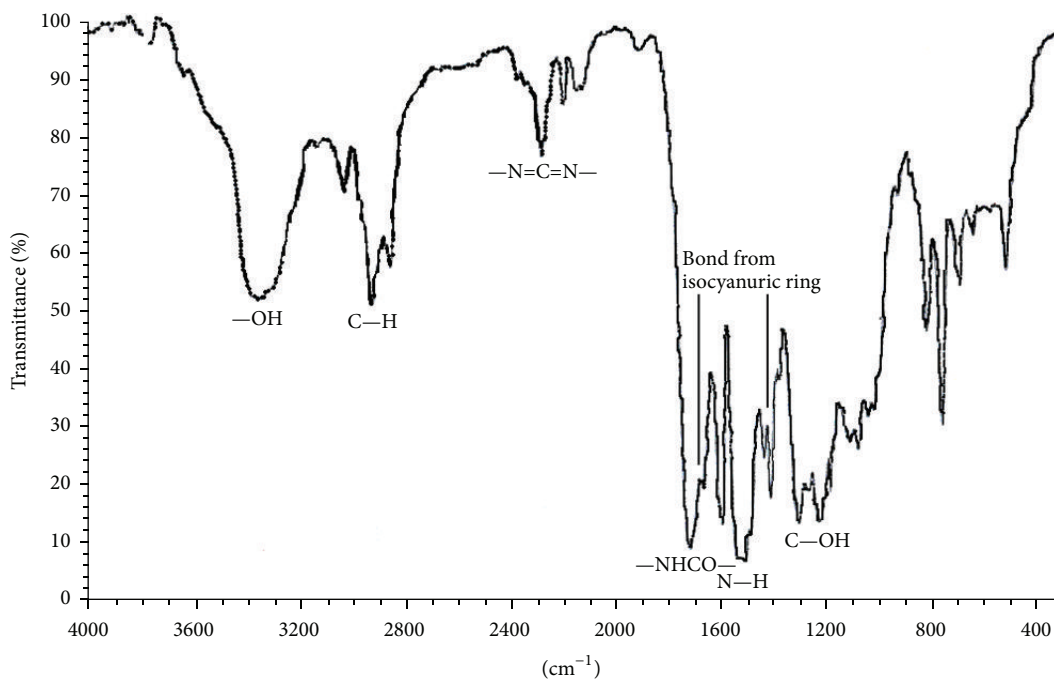


FIGURE 1: IR spectrum of standard PUR-PIR foam.

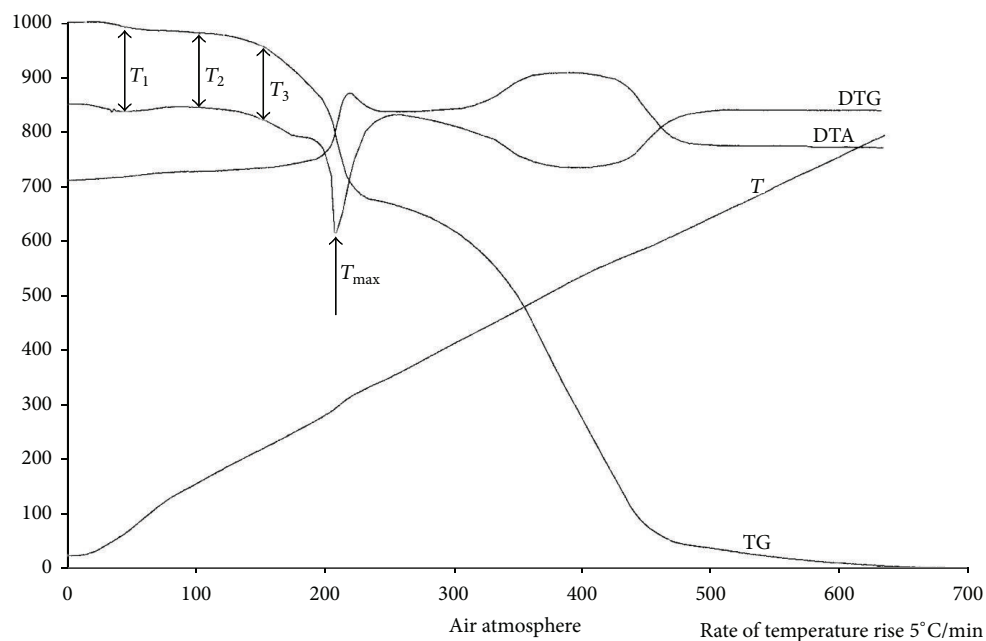


FIGURE 2: Example of thermogram of rigid PUR-PIR foam. Notations of symbols are provided in text.

of recycle obtained from foam with addition of 15% *w/w* of polyethylene glycol were characterized by the lowest brittleness, that is, 18.4%. Softening point of standard foams (without recycle added, foam 0) was 230.0°C. As the content of recycles was increased in foam composition from 0.1 to 0.4 of chemical equivalent, softening point decreased from 230°C (foam 0) to 228.9°C (foam 4), 226.1°C (foam 8), 222.3°C (foam 12), 218.9°C (foam 16), 216.4°C (foam 20), 214.1°C (foam

24), 224.1°C (foam 28), 211.9°C (foam 32), and 209.7°C (foam 36, Table 6), respectively.

Supreme effect on reduction of flammability had the addition of glycolysis products obtained from foams with addition of 15% *w/w* of polyethylene glycol 1500 (foams 25–28).

Flammability of these foams decreased what was manifested by increase of oxygen index and retention from 22.1%

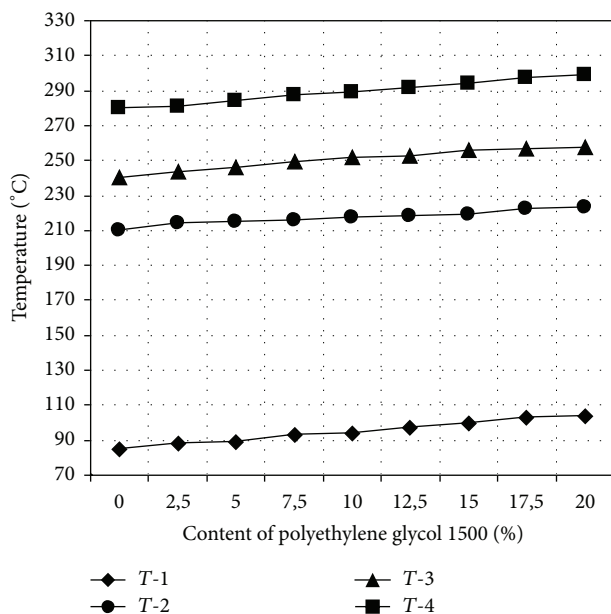


FIGURE 3: Dependence between temperature of decomposition of rigid PUR-PIR foams and content of polyethylene glycol 1500. T_1 —temperature of the first loss of foam mass °C, T_2 —extrapolated temperature of the beginning of the first loss of foam mass °C, T_3 —temperature of the beginning of rapid decomposition °C, and T_4 —temperature of the highest rate of loss of foam mass °C.

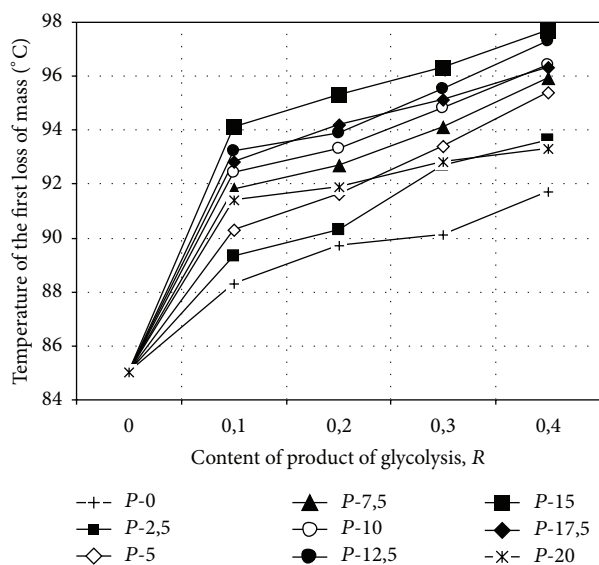


FIGURE 4: Dependence between the first loss of mass of rigid PUR-PIR foams and content of product of glycolysis.

and 76.6% (standard foams, 0) to 25.1% and 86.4% (foam 28), respectively. The lowest effect on flammability has addition of glycolysis products in amounts of 2.5% w/w , 5% w/w , and 7.5% w/w .

It was found that addition of recyclates had no effect on percentage change of volume and percentage of mass loss of the new foams.

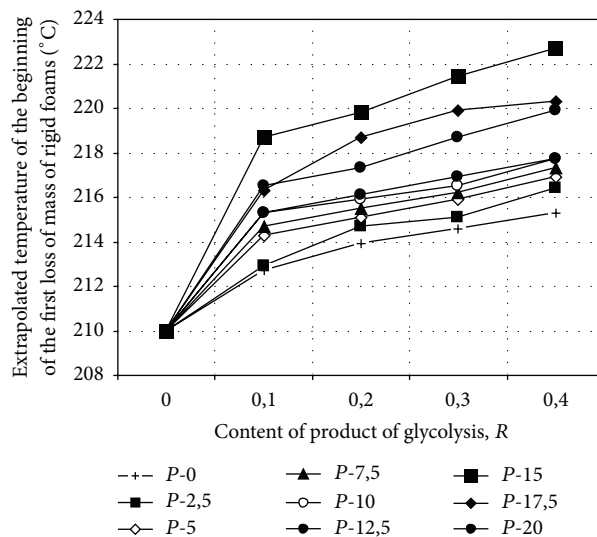


FIGURE 5: Dependence between extrapolated temperature of the beginning of the first loss of mass of rigid PUR-PIR foams and content of product of glycolysis.

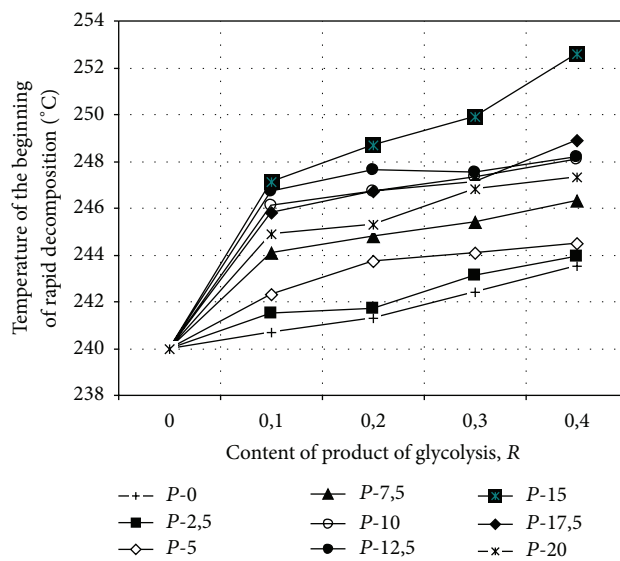


FIGURE 6: Dependence between temperature of the beginning of rapid decomposition of rigid PUR-PIR foams and content of product of glycolysis.

Increasing of the recycle content in new foams from 0.1 to 0.4 of chemical equivalent resulted in the highest increase of T_1 , T_2 , T_3 , and T_4 in the case of addition of recycle obtained by glycolysis of foams with addition of 15.0% w/w of polyethylene glycol (foams 25–28 according to Table 5, Figures 3–6). The parameters of foams increased as follows: temperature of the first mass loss from 85°C (foam 0) to 97.3°C (foam 28, Table 5, Figure 3), extrapolated temperature of the beginning of the first mass loss from 210°C (foam 0) to 222.7°C (foam 28, Figure 4), temperature of the beginning of rapid decomposition from 240°C (foam 0) to 252.6°C (foam

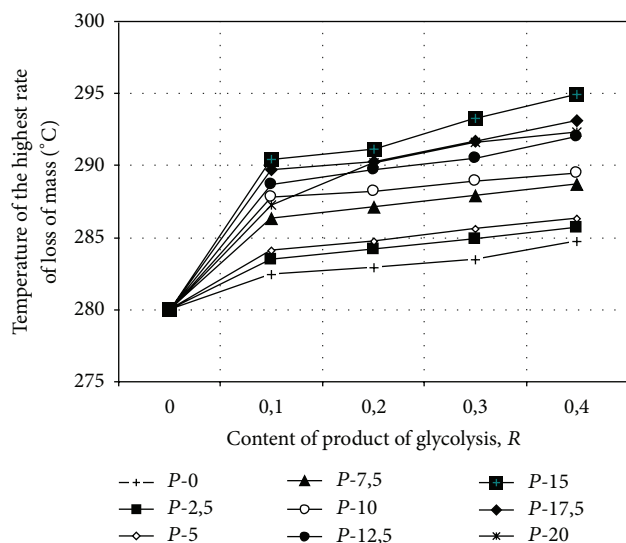


FIGURE 7: Dependence between temperature of the highest rate of loss of mass of the rigid PUR-PIR foams and content of product of glycolysis.

28, Figure 5), and temperature of the highest rate of mass loss from 280°C to 294.9°C (foam 28, Figure 6).

Addition of recyclates obtained from foam without polyethylene glycol 1500 (foams 1–40, Table 5) has a slight effect on thermal resistance of the new foams (Figures 3–7).

4. Summary

Rigid polyurethane-polyisocyanurate foams were prepared by one-stage method at equilibrium ratio of NCO:OH groups equal to 3:1, with addition of polyethylene glycol. Waste foams were subjected to chemical recycling (glycolysis). The obtained products of glycolysis, after the determination of basic properties (hydroxyl number) required to define the recipe, were applied to prepare the new foams.

It was found that the use of polyethylene glycol had an effect on reduction of brittleness, softening point, and increase of compressive strength. Maximum reduction of foam flammability in comparison to standard foam (the highest retention and oxygen index) was observed in the foams with the highest content of polyethylene glycol. Introducing polyethylene glycol 1500 in amount from 0% to 20% w/w into rigid PUR-PIR foams had a slight effect on their thermal resistance determined by the method of thermogravimetric analysis. Polyethylene glycol 1500 fulfills the role of reactive filler in foam.

Glycolysis of waste foams with addition of polyethylene glycol proceeded without disturbances. After 4 hours lasting glycolysis, the liquid products were obtained which, after the determination of hydroxyl number, were applied to prepare the new foams. Addition of the obtained products of glycolysis has an effect on physicochemical properties of foams. Foams obtained from products of glycolysis with 15% w/w of polyethylene glycol 1500 were characterized by the best properties in comparison with standard foam (with

no recycle added). As the amount of recycle was increased in foam composition from 0.0 to 0.4 of chemical equivalent, at simultaneous decrease of Rokpol RF-55 by the same quantity, apparent density, compressive strength, oxygen index, retention, and thermal resistance (thermogravimetric analysis) increased and brittleness decreased. Thus, products of glycolysis can be successfully applied to prepare the new foams. When they are applied as polyol in polyurethane premix, they react with polyisocyanate with formation of macromolecular polyurethane.


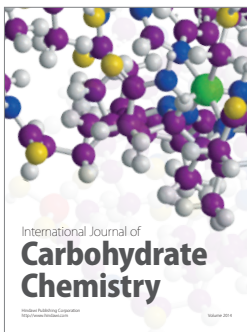
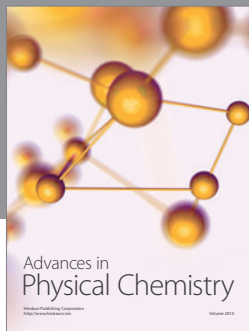
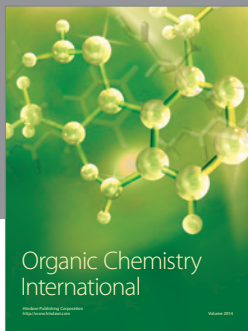
Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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