Macromolecular Research **Article**

DOI 10.1007/s13233-019-7068-6 www.springer.com/13233 pISSN 1598-5032 eISSN 2092-7673

Polyurethane Foams with 1,3,5-Triazine Ring and Silicon Atoms

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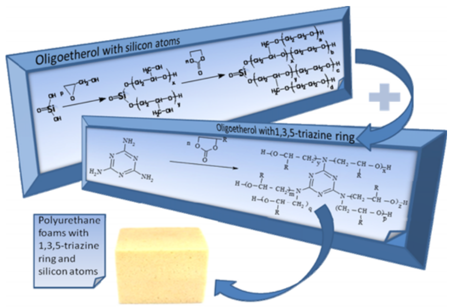
Received May 15, 2018 / Revised October 26, 2018 / Accepted October 28, 2018

Abstract: The method of obtaining polyurethane foams based on two oligoetherols, synthesized from (1) melamine and propylene carbonate, and (2) from metasilicic acid, glycidol and ethylene carbonate, is elaborated. The physical properties of PUFs are tested depending on composition of oligoetherol substrates mixture used. It has been found that 1,3,5-triazine rings in PUF increase their thermal resistance, while silicon contributes to improvement of mechanical properties of PUF. The silicon-modified PUFs can stand long term heating at 150-200 °C with concomitant increase of compression strength and decrease of flammability of PUFs. The PUFs heated at 150 °C for one month become self-extinguishing, or even inflammable upon exposure at 175 °C.



Keywords: metasilicic acid, melamine, hydroxyalkylation, polyurethane foams, properties.

1. Introduction

Polyurethanes are useful materials applied often in daily life due to their chemical resistance to diluted acids and bases, oils, lubricants, organic solvents, atmospheric components, and to their suitable plasticity, high hardness and resistance to attrition. They are fabricated as rubbers, glues, lacquers, or fibers, and the most but not least as polyurethane foam (PUFs). 80% of polyurethanes are used as PUFs.[1] However, traditional rigid PUFs lose their properties upon thermal exposure above 90 °C.[2] Also they are flammable and not thermally resistant. Therefore, it is crucial to improve their thermal properties. One of the methods to improve thermal resistance of PUFs is based on modification of oligoetherol substrate incorporated with thermally resistant ring, such as 1,3,5-triazine or perhydro-1,3,5-triazine, purine, pyrimidine, or carbazole.[3-7] An effective way to reduce the flammability of polyurethane foams is to incorporate phosphorus, chlorine, bromine or boron atoms into their structure.[8] Another possibility to increase mechanical and thermal resistance of PUFs is chemical introduction of silicone into their structure. There are not many reports on this subject.[9] Mostly the silicon is introduced into PUFs at the foaming step, as additive nano-sized modifier. The addition of silicon into PUF resulted in improvement of mechanical and thermal properties of PUF, although deterioration of pore formation of PUF is disadvantage.[10-15] It has also been demonstrated that the addition of a small amount of reactive silicon compounds may improve both mechanical and thermal resistance of PUFs. In such modified PUFs the silicon resulted in increased thermal stability of decreased flammability of PUF. The latter is presumably due to layering of silicon dioxide on the surface of PUF, making the layer heat insulator. Moreover, the silicon-modified PUFs do not emit smoke upon flaming.[12-15] Recently, the silsesquioxanes were used as PUF modifiers leading to improvement of thermal resistance of PUF. Silsesquioxanes have terminal hydroxyl groups which react with isocyanate groups of urethane prepolymers to give final polyurethanes of enhanced thermal stability.[16-19] Hybrid foams formed from polyurethane and polysiloxanes are better heat isolator than classic PUFs.[20] The method of hydroxyalkylation of metasilicic acid with glycidol (GL) and ethylene carbonate (EC) to give H_2SiO_3:GL:EC=1:4:3 stoichiometry oligoetherol suitable for obtaining PUFs has been explored.[21]

The PUFs obtained in this way revealed all properties similar to classic rigid PUFs, except enhanced thermal resistance and improved mechanical properties. They could withstand long term heating at 175 °C, and additionally, they gain compression strength after thermal exposure. We have also elaborated the method of obtaining PUFs with 1,3,5-triazine ring.[22] They were obtained from an oligoetherol synthesized from melamine (MEL) and propylene carbonate (PC) at MEL:PC=1:20 molar ratio. They could withstand long term heating at 200 °C.

Here we report our attempts to obtain PUFs bearing both high thermal resistance and improved mechanical resistance. We have synthesized both mentioned oligoetherols, and examined the properties of PUFs obtained from thereof. They were compared with the properties of foams synthesized from melamine and propylene carbonate as well as from silicic acid, glycidol and ethylene carbonate, as previously described.[21,22] We also monitored the changes of the obtained PUF after exposure to elevated temperatures.

2. Experimental

2.1. Syntheses

The oligoetherol with incorporated silicon was synthesized from metasilicic acid, glycidol (GL) and ethylene carbonate (EC) as

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*Corresponding Author: Jacek Lubczak (jml@prz.edu.pl) before.[21] Obtained oligoetherol contained the components at H_2SiO_3:GL:EC=1:4:3 molar ratio and 9.5 mass % of dispersed poly(metasilicic acid) (Scheme 1):

The oligotherol with 1,3,5-triazine ring was obtained from MEL and PC at 1:20 molar ratio as described before[22] (Scheme 2).

2.2. Mixture of oligoetherols

66.6 g (0.14 mol) of H_2SiO_3:GL:EC=1:4:3 oligoetherol and 133.4 g (0.12 mole) of oligoetherol obtained from MEL:PC=1:20 were placed in 500 cm^3 round bottom flask equipped with reflux condenser, mechanical stirrer and thermometer. The mixture was stirred and heated at 80 °C for 20 min. The homogeneous mixture composed of 33.3% (H_2SiO_3:GL:EC=1:4:3) and 66.7% (MEL:PC=1:20) was obtained. In the same way the mixture composed of 50.0% (H_2SiO_3:GL:EC=1:4:3) and 50.0% (MEL: PC=1:20), and 66.7% (H_2SiO_3 :GL: EC=1:4:3) and 33.3% (MEL: PC=1:20) were obtained using 100 g (H_2SiO_3:GL:EC=1:4:3) and 100 g (MEL:PC=1:20), and 133.4 g (H_2SiO_3:GL:EC=1:4: 3) and 66.7 g MEL:PC=1:20, respectively.

2.3. Obtaining of polyurethane foams

Oligoetherol foaming was performed in 500 cm^3 cups at room temperature as follows: 10 g mixtures of oligoetherols, 0.19-0.23 g surfactant (Silicon L-6900, pure, Momentive, USA), 3-4 wt% water and 0.0-0.16 g triethylamine (TEA, pure, Fluka, Switzerland) as catalyst related to oligoetherol. Then polymeric diphenylmethane 4,4'-diisocyanate (pMDI, prod. Merck, Germany) was added and the mixture was vigorously stirred until creaming started. The PUFs were seasoned for 4 days, after which the samples were cut off and subjected to further studies.

2.4. Properties of foams

The apparent density,[23] water uptake,[24] dimensional stability in 150 °C temperature,[25] heat conductance coefficient (IZOMET 2104, Slovakia), and compressive strengt[26] of PUFs with flame retardants were measured. Thermal resistance of modified foams was determined, static and dynamic methods. In static method, the foams were heated at 150, 175 and 200 °C with continuous measurement of mass loss and determination of mechanical properties before and after heat exposure. In dynamic method, thermal analyses of foams were performed in ceramic crucible at 20-600 °C temperature range, about 100 mg sample, under air atmosphere with Thermobalance TGA/DSC 1 derivatograph, Mettler, with 10 °C/min heating rate. Differential scanning calorimetry (DSC) studies were done with DSC822^e Mettler Toledo calorimeter at 20-300 °C temperature range, 10 deg/min heating rate, 10-20 mg samples under nitrogen atmosphere. Flammability of foams was determined by oxygen index and horizontal test according to a previous study[27] as follows: the foam samples (150×50×13 mm) were weighed, located on horizontal support (wire net of 200×80 mm dimensions) and the line was marked at the distance of 25 mm from edge. The sample was set on fire from the opposite edge using Bunsen burner with the blue flame of 38 mm height for 60 s. Then the burner was removed and time of free burning of foam reaching marked line or cease of flame was measured by stopwatch. After that the samples were weighed again. The rate of burning was calculated using the equation:

$$v = \frac{125}{t_b} \tag{1}$$

if the sample was burned totally, or using the equation:

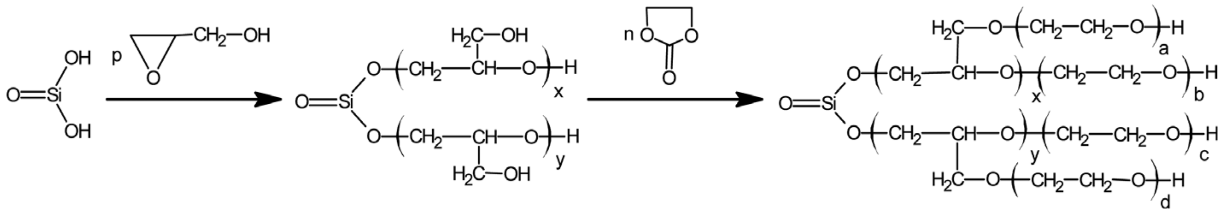
$$v = \frac{L_e}{t_e} \tag{2}$$

if the sample ceased burning, where:

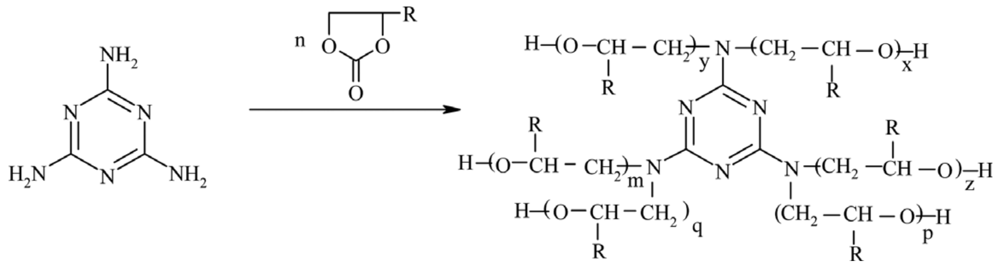
L_e-the length of burned fragment, measured as the difference 150 minus the length of unburned fragment (in mm). If the burned fragment has the 125 mm length, the foam was considered as flammable.

t_b, t_e-the time of propagation of flame measured at the distance between starting mark up to the end mark or as the time of flame cease.

The mass loss Δ m after burning was calculated from the equation:



Scheme 1. Reaction of metasilicic acid with excess of glycidol and ethylene carbonate.



Scheme 2. Obtaining of oligoetherol from melamine and propylene carbonate, where: x + y + z + p + q + m = n R = $-CH_3$.

$$\Delta m = \frac{m_o - m}{m_o} \cdot 100\% \qquad (3)$$

where m_o and m - mean the sample mass before and after burning, respectively.

Flammability of foams were evaluated for samples 100×100 ×10 mm in size using a cone microcalorimeter, a product of FTT Ltd. (United Kingdom), according to standard,[28] by applying the heat flow 25 kW/m^2 and the distance from ignition source 25 mm. During the tests the time to ignite (TTI), total time of flaming (TTF), percentage mass loss (PLM), heat release rate (HRR), effective heat of combustion (EHC) and total heat release (THR) were recorded. The morphology of PUFs was investigated by an optical microscope Nikon Eclipse LV100 POL, using a digital camera Sight DS-5Mc at 5 or 10-fold magnification.

3. Results and discussion

The mixture of oligoetherols was used to obtain polyurethane foams. The foaming was optimized with catalyst, isocyanate, and water. The amount of isocyanate was initially calculated based upon experimentally determined hydroxyl number of oligoetherols (Table 1) and then adjusted for optimization. Finally, it was found that the amount of isocyanate correlated with the number of hydroxyl equivalents by 1.6-2.2 (isocyanate coefficient, Table 2, col. 7). The amount of water as foaming agent depended on the kind of oligoetherol. The best PUFs were obtained when 3% of water in relations to mass of oligoetherol composition 66.7% (H_2SiO_3:GL:EC=1:4:3) and 33.3% (MEL:PC=1:20) was used. In other cases the optimized water amount was 4 %. The amount of catalyst (TEA) was 0.7 and 0.8% for oligoetherol compositions: 66.7% (H_2SiO_3:GL:EC=1:4:3) and 33.3% (MEL :PC=1:20), and 50.0% (H_2SiO_3:GL:EC=1:4:3) and 50.0% (MEL:PC=1:20), respectively. The oligoetherol composition: 33.3% (H_2SiO_3: GL:EC =1:4:3) and 66.7% (MEL:PC=1:20) did not require catalyst (Table 2, col. 4). Optimized surfactant amount was 1.9% (Table 2, col. 5). Cream time for optimized foams was within 21-54 s, rise time was 19-55 s, and tack free time was 2-100 s. All these time parameters were the longest for compositions containing the largest percentage of silicon (Table 2, col. 8-10).

Physical properties for optimized foams were studied. Apparent density of PUFs was within 42.2-73.2 kg/m^3 (Table 3, col. 3). The PUFs showed slight shrinkage (reaching up to-1.79%) upon thermal exposure at 150 °C (Table 4, col. 2-7), while water uptake after 24 h was maximally 5.4-6.2% for PUFs with larger amount of Si (Table 3, col. 6). This indicates that PUFs have closed pores, based on morphology analysis (vide infra). Heat conductance coefficient of obtained PUFs is into 0.0314-0.0395 W/m·K region, which is slightly higher in comparison with that of classic PUFs. After thermal exposure of PUFs it raises considerably with increase of thermal exposure, which is due to pore opening and other structural changes in PUF (Table 3, col. 7). It correlates also with increased water uptake (Table 3, col. 4-6).

Static tests on thermal resistance of obtained PUFs were performer at 150, 175, and 200 °C by measuring mass loss with concomitant control of physical properties. The largest mass loss of PUFs was observed at the first day of the test (Figure 1). We have found that the PUF thermal resistance is higher when the composition contains more 1,3,5-triazine rings. Introduction of silicon resulted in decrease of thermal resistance of PUFs. Thus the PUFs obtained from mixture of oligoetherols with 33.3% or 66.7% (H_2SiO_3:GL:EC=1:4:3) lost 2.9 or 6.0% higher mass loss than the corresponding PUFs obtained from MEL:PC=1:20 oligoetherol, without silicon incorporated[22] (Table 5). Thermal resistance of silicon-modified PUFs at 175 °C thermal resistance was 6.4-7.2% lower, while at 200 °C it was only 1.1-3.5% lower.

It is noteworthy that obtained PUFs showed increased compression strength after thermal exposure (Table 5, col. 4). That was not observed in case of PUFs obtained from MEL and PC based oligoetherols. Generally the annealing of PUFs can prolongate the crosslinking of PUFs, which causes increase of compressive strength. A considerable increase of compressive strength upon annealing was noticed for PUFs modified with large silicon participation in PUFs. Increased compression strength of silicon-containing PUFs after thermal exposure can be attributed to presence of stable Si-O bonds rendering the foam rigid. Recently obtained PUFs based exclusively on silicon-oligoetherols showed lower thermal resistance but larger increase of compressive strength upon annealing (especially for composition foamed with 2% water.[21]

Thermal resistance of obtained PUFs was also examined by DSC before thermal exposure. All the samples of PUFs obtained here showed the mass loss already within 35-110 °C in the first

Table 1. Hydroxyl numbers of obtained for different oligoetherols

Oligoetherol	Hydroxyl number (mg KOH/g)
33.3% (H_2SiO_3:GL:EC=1:4:3) +66.7% (MEL:PC=1:20)	457.3
50.0% (H_2SiO_3:GL:EC=1:4:3) +50.0% (MEL:PC=1:20)	545.3
66.7% (H_2SiO_3:GL:EC=1:4:3) +33.3% (MEL:PC=1:20)	546.0

Table 2. The influence of oligoetherol composition on foaming process

Oligoetherol	Composition [g/100 g of oligoetherols]					Foaming process		
	Isocyanate	CatalystTEA	Silicone L-6900	Water	Isocyanate index	Cream time (s)	Rise time (s)	Tack free time (s)
33.3% (H_2SiO_3:GL:EC=1:4:3) +66.7% (MEL:PC=1:20)	210	0.0	1.9	4	2.2	32	38	2
50.0% (H_2SiO_3:GL:EC=1:4:3) +50.0% (MEL:PC=1:20)	220	0.8	1.9	4	2.1	21	19	12
66.7% (H_2SiO_3:GL:EC=1:4:3) +33.3% (MEL:PC=1:20)	190	0.7	1.9	3	1.6	54	55	100

*Composition obtained under optimized foaming conditions.

Table 3. Physical properties of polyurethane foams

Oligoetherol	Foam	Density (kg/m^3)	Water uptake (%wt) after 5 min	3 h	24 h	Heat conductance coefficient (W/m·K)
33.3% (H_2SiO_3:GL:EC=1:4:3) +66.7% (MEL:PC=1:20)	Before exposure	42.17	0.73	1.40	2.22	$0.0325\pm2.50\cdot10^{-4}$
	After exposure in temperature 150 °C	35.72	1.60	2.36	3.12	$0.0553\pm5.09\cdot10^{-4}$
	After exposure in temperature 175 °C	33.84	2.54	3.79	5.50	$0.0508\pm2.03\cdot10^{-4}$
	After exposure in temperature 200 °C	39.59	3.59	6.20	8.14	$0.0776\pm2.33\cdot10^{-4}$
50.0% (H_2SiO_3:GL:EC=1:4:3) +50.0% (MEL:PC=1:20)	Before exposure	73.17	2.40	4.34	6.23	$0.0395\pm9.48\cdot10^{-5}$
	After exposure in temperature 150 °C	66.87	4.13	6.06	10.35	$0.0418\pm1.29\cdot10^{-4}$
	After exposure in temperature 175 °C	68.78	4.57	8.02	14.33	$0.0482\pm6.27\cdot10^{-4}$
	After exposure in temperature 200 °C	76.43	6.21	10.07	15.30	$0.6280\pm9.42\cdot10^{-4}$
66.7% (H_2SiO_3:GL:EC=1:4:3) +33.3% (MEL:PC=1:20)	Before exposure	50.35	2.20	3.20	5.40	$0.0314\pm9.11\cdot10^{-5}$
	After exposure in temperature 150 °C	53.29	3.75	5.86	8.23	$0.0678\pm8.54\cdot10^{-4}$
	After exposure in temperature 175 °C	55.76	4.72	8.63	12.21	$0.0486\pm8.26\cdot10^{-5}$
	After exposure in temperature 200 °C	64.10	16.1	22.30	30.16	-

Apparent density and water uptake were determined with ± 2% accuracy

Table 4. Dimension stability of foams

Polyurethane foam obtained from oligoetherol	Dimensional stability (%) in temperature 150 °C					
	Length change (%)		Width change (%)		Hight change (%)	
	20 h	40 h	20 h	40 h	20 h	40 h
33.3% (H_2SiO_3:GL:EC=1:4:3)+66.7% (MEL:PC=1:20)	-0.66	-0.85	-1.79	1.55	1.20	0.84
50.0% (H_2SiO_3:GL:EC=1:4:3)+50.0% (MEL:PC=1:20)	-0.25	-0.27	0.12	-0.52	0.12	-0.10
66.7% (H_2SiO_3:GL:EC=1:4:3)+33.3% (MEL:PC=1:20)	1.10	0.88	-1.14	-1.57	0.77	0.38

Dimensional stability was determined with ± 1.5% accuracy

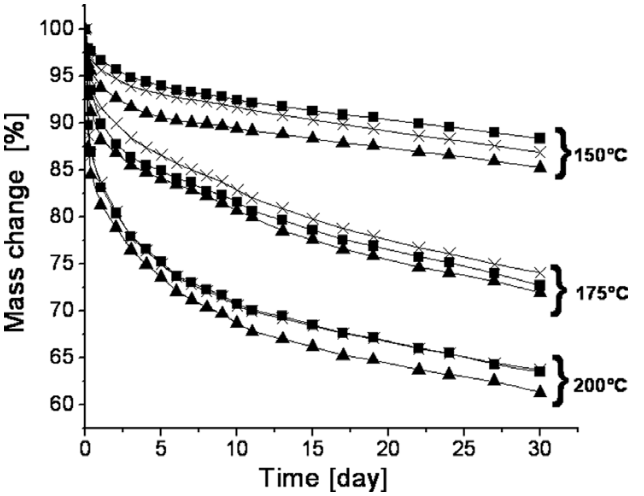


Figure 1. Thermal stability of the polyurethane foams, determined by the mass loss after heating at high temperature 150, 175 and 200 °C. Polyurethane obtained from oligoetherols: (–■–) 33.3%(H_2SiO_3:GL:EC=1:4:3)+66.7% (MEL:PC=1:20), (–×–) 50.0%(H_2SiO_3:GL:EC=1:4:3)+50.0%(MEL:PC=1:20), (–▲–) 66.7%(H_2SiO_3:GL:EC=1:4:3)+33.3%(MEL:PC=1:20).

cycle of heating. The endothermic peaks within that region of temperature was due to the presence of water absorbed from atmosphere. In the second cycle the peaks were not observed. It was however observed again at the same temperature as in the first cycle after exposure of samples to atmosphere for one day. Because the mass loss of sample of approx. 5% occured early in the process, which is usually the parameter characterizing thermal resistance, we have used another parameter, i.e. 10% mass loss, which obviously can be registered at higher temperatures, where no peak of water mass loss is noticed. It was found that the temperature of the initial (10%) foam weight loss is the highest in the foam containing the largest share of 1,3,5-triazine rings and is 246 °C (Table 6). Considering the profile of mass loss, the fastest degradation was observed at 284-315 °C. Presumably it was related with the degradation of oxyalkylene chains. At 390 °C the second maximum of degradation rate was observed, which might related Si-O skeleton bonds disruption.

Thermal resistance of annealed PUFs was studied by dynamic method. It showed that they decomposed at higher temperatures than that of corresponding not-annealed PUFs. Moreover, the higher annealing temperature caused a higher temperature of 10% weight loss (Table 6). Finally, the 50% mass loss of PUFs exposed for one month at 175 °C was observed at temperatures above 600 °C.

All PUFs were flammable. The rate of flaming of PUF obtained from oligoetherol 33.3% (H_2SiO_3:GL:EC=1:4:3) and 66.7% (MEL:PC=1:20) was 9.7 mm/s, i.e. higher than that of PUF obtained from oligoetherol MEL:PC=1:20 (6,2 mm/s, Table 7). Other PUFs, containing more silicon flamed with 3.1-4.8 mm/s rate. The mass loss after total flaming was 58.0-64.2%, as it was found in horizontal test. It corroborate well with the values of oxygen index which was within 20.0-20.4% (Table 5, col. 9). Oxygen index of PUF before and after annealing was also determined. It has been found that oxygen index of PUFs increased upon annealing. The annealed PUFs smoked less during flaming test than not-annealed ones. The PUFs annealed for one month at 175 °C barely glow after flame initiation at oxygen index 43%. Thus annealed PUFs showed decreased flammability, which is advanta-

Table 5. Thermal stability, compressive strength and flame properties of foams.

Polyurethane foam obtained from oligoetherol	Foam	Mass loss in % wt. after exposition in month	Compressive strength [MPa]	Flame zone [mm]	Flame rate [mm/s]	Mass loss upon flaming [%]	Remarks	Oxygen index
33.3% (H_2SiO_3:GL:EC=1:4:3) +66.7% (MEL:PC=1:20)	Before exposure	0.00	0. 157	150.0	9.74	61.21	Flammable	20.0
	After exposure in temperature 150 °C	11.62	0.241	8.3	0.32	0.02	Self extinguishing	23.6
	After exposure in temperature 175 °C	27.29	0.389	0.0	0.0	0.0	The foam does not ignite in the flame of the burner	43.0
	after exposure in temperature 200 °C	36.50	0.182	0.0	0.0	0.0	The foam does not ignite in the flame of the burner	56.8
50.0% (H_2SiO_3:GL:EC=1:4:3) +50.0% (MEL:PC=1:20)	Before exposure	0.00	0.282	150.0	3.09	57.97	Flammable	20.4
	After exposure in temperature 150 °C	13.11	0.320	0.0	0.0	0.0	The foam does not ignite in the flame of the burn	23.6
	after exposure in temperature 175 °C	25.75	0.326	0.0	0.0	0.0	The foam does not ignite in the flame of the burn	43.0
	After exposure in temperature 200 °C	36.25	0.388	0.0	0.0	0.0	The foam does not ignite in the flame of the burn	56.5
66.7% (H_2SiO_3:GL:EC=1:4:3) +33.3% (MEL:PC=1:20)	Before exposure	0.00	0.286	150.0	4.76	64.19	Flammable	20.3
	After exposure in temperature 150 °C	14.73	0.425	0.0	0.0	0.0	Self extinguishing	22.5
	After exposure in temperature 175 °C	28.05	0.704	0.0	0.0	0.0	The foam does not ignite in the flame of the burn	43.0
	After exposure in temperature 200 °C	38.69	0.485	0.0	0.0	0.0	The foam does not ignite in the flame of the burner	56.8
MEL:PC=1:20 [22]	Before exposure	0.00	0.43	150	6.2	-	-	-
	After exposure in temperature 150 °C	8.73	0.47	-	-	-	-	-
	After exposure in temperature 175 °C	20.86	0.43	-	-	-	-	-
	After exposure in temperature 200 °C	35.21	0.20	-	-	-	-	-
H_2SiO_3:GL:EC=1:4:3, composition with 2% H_2O[21]	Before exposure	0.00	0.486	150	2.03	100	Melts, drips	21.1
	After exposure in temperature 150 °C	24.00	1.275	105	2.1	2.45	Self extinguishing	24.4
	After exposure in temperature 175 °C	30.90	5.051	0.0	0.0	0.47	The foam does not ignite in the flame of the burn	36.0
H_2SiO_3:GL:EC=1:4:3, composition with 4% H_2O[21]	Before exposure	0.00	0.167	21	0.7	16.8	Self extinguishing	21.9
	After exposure in temperature 150 °C	1.67	0.321	0.0	0.0	5.62	Burns in flame, extinguish out of flame	23.4
	After exposure in temperature 175 °C	36.50	0.360	0.00	0.00	2.52	The foam does not ignite in the flame of the burn	38.0

Table 6. Thermal analysis of foams determined by dynamic method

Polyurethane foam obtained from oligoetherol	Foam No	$T_{10\%}$ (°C)	$T_{25\%}$ (°C)	$T_{50\%}$ (°C)	T_{max} (°C)
33.3% (H_2SiO_3:GL:EC=1:4:3)+66.7% (MEL:PC=1:20)	1	246	285	352	284
50.0% (H_2SiO_3:GL:EC=1:4:3)+50.0% (MEL:PC=1:20)	2	223	282	334	315
2 after exposure in temperature 150 °C	2a	256	328	438	347
2 after exposure in temperature 175 °C	2b	295	438	>600	380
2 after exposure in temperature 200 °C	2c	300	478	>600	380
66.7% (H_2SiO_3:GL:EC=1:4:3)+33.3% (MEL:PC=1:20)	3	223	271	323	300

geous property of these materials. Elemental analysis of annealed PUFs (Table 8) demonstrated the decrease of H percentage, and relative increase of N percentage. These composition changes are responsible for restricted flammability of annealed PUFs.

Structural changes in annealed PUFs were monitored by IR spectroscopy (Figure 2). Not exposed PUFs showed the N-H stretching vibration at 3400 cm^{-1} and bending band within 1600-1537 cm^{-1} (II amide band). The carbonyl stretching band

Table 7. Comparison of flame properties of foams

Foam obtained from oligoetherol	Flame zone (mm)	Flame rate (mm/s)	Mass loss upon flaming (%)
33.3% (H_2SiO_3:GL:EC=1:4:3)+66.7% (MEL:PC=1:20)	150	9.7	61.2
50.0% (H_2SiO_3:GL:EC=1:4:3)+50.0% (MEL:PC=1:20)	150	3.1	58.0
66.7% (H_2SiO_3:GL:EC=1:4:3)+33.3% (MEL:PC=1:20)	150	4.8	64.2
MEL:PC=1:20[22]	150	6.2	-
H_2SiO_3:GL:EC=1:4:3 (4% H_2O)[21]	21	0.7	16.8
H_2SiO_3:GL:EC=1:4:3 (2% H_2O)[21]	150	2.0	100

Table 8. Elemental analysis of foam obtained from mixture of oligoetherols 50.0% (H_2SiO_3:GL:EC=1:4:3)+50.0% (MEL:PC=1: 20)

Foam	Element		
	N	C	H
Before exposure	9.21	65.50	5.69
After exposure in temperature 150 °C	9.63	64.04	5.07
After exposure in temperature 175 °C	10.50	63.41	4.09
After exposure in temperature 200 °C	11.32	61.92	3.63

(I amide band) was localized at 1727 cm^{-1}. Ester C-O bond is visible at ca 1200cm^{-1} The C-H stretching bands were observed within 3000-2900 cm^{-1}, while deformation methylene band was found at 1465 cm^{-1}. Unreacted isocyanate groups were identified by the presence of characteristic band at 2276 cm^{-1}, while carbodiimide band was observed at 2136 cm^{-1}. Upon heating at 150 °C there were characteristic changes in IR spectra of PUFs, namely the disappearance of carbodiimide bands as well as isocyanate group band. We attribute the latter to oxidation and further conversion of isocyanate by reaction with remaining hydroxyl groups. That suggests the additional crosslinking of foam at this temperature took place which corroborate well with increase of compression strength upon annealing. In the spectrum of PUF annealed at 200 °C the band centered at 1660 cm^{-1} was attributed to formation of C=C double bonds related to carbonization of PUF (Figure 3). Also the C-H valence bands within broad region 3300-2500 cm^{-1} a deformation =C-H bands within 1000-650 cm^{-1} were present. The 1,3,5,-triazine ring band at 834 cm^{-1}, remained intact in annealed PUFs.

The PUFs were microscopically examined with Nicon Eclipse LV 100 POL in order to observe the morphology of PUFs before

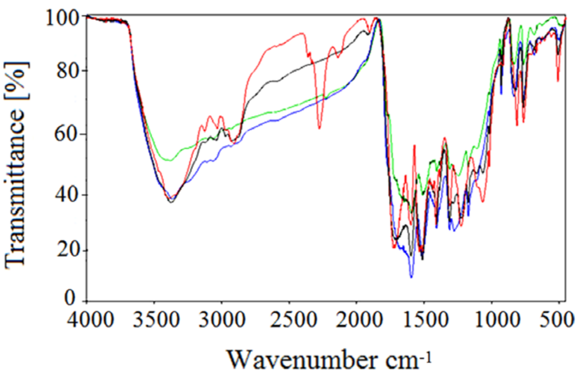


Figure 2. IR spectra of foams obtained from oligoetherol 50.0% (H_2SiO_3:GL:EC=1:4:3) and 50.0% (MEL:PC=1:20) before exposure (red) and after exposure in temperature 150°C (black), 175 °C (blue) and 200 °C (green).

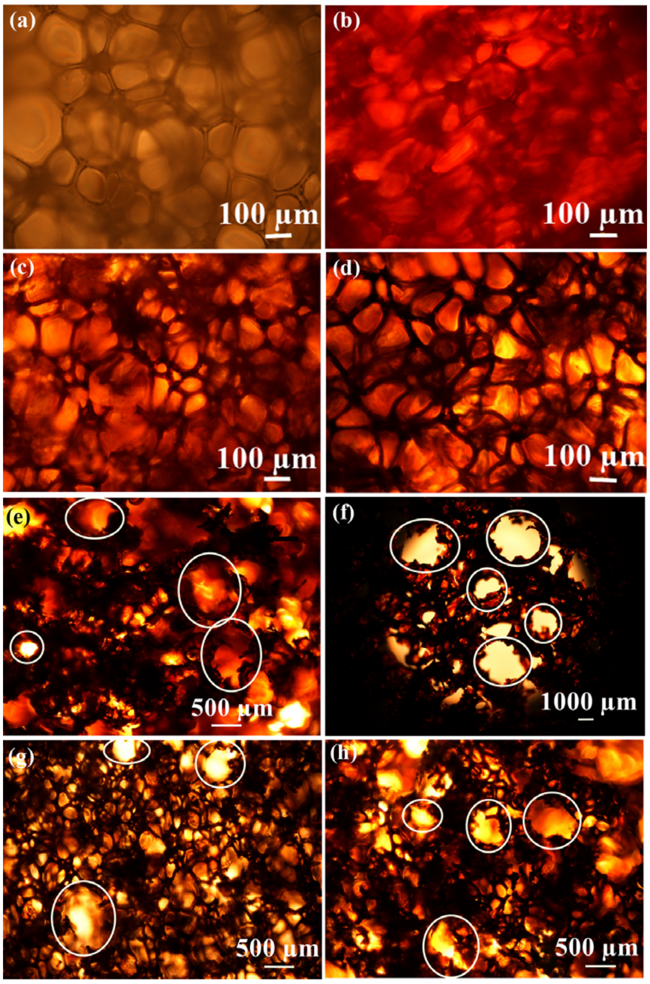


Figure 3. Digital image of foam obtained from oligoetherol 33.3% (H_2SiO_3:GL:EC=1:4:3) and 66.7% (MEL:PC=1:20) (lens magnification 10) unexposed (a) and after exposure in temperature 150 °C (b), 175 °C (c) and 200 °C (d) and from oligoetherol 50.0% (H_2SiO_3:GL:EC=1:4:3) and 50.0.% (MEL:PC=1:20) after exposure in temperature 175 °C (e) and 200 °C (f) and from oligoetherol 66.7% (H_2SiO_3:GL:EC=1:4:3)+33.3% (MEL:PC=1:20) after exposure in temperature 175 °C (g) and 200 °C (h).

and after thermal exposure The pore diameters of PUFs before thermal exposure was 280-320 µm (Figure 3(a)-(d) for the foam obtained from oligoetherol 33.3% (H_2SiO_3:GL:EC=1:4:3) and 66.7% (MEL:PC=1:20)) with exception of PUF obtained from mixture of oligoetherols 50.0% (H_2SiO_3:GL:EC=1:4:3) and 50.0% (MEL:PC=1:20) for which 1000 µm diameter pores were observed. Generally annealing of PUFs resulted in decrease of size of pores. Another observation led to conclusion that annealing of PUFs at 200 °C lead to partial carbonization of PUF, which is demon-

Table 9. Flame retardance studies of PUFs measured by cone microcalorimeter

Foam	TTI (s)	TTF (s)	PML (%)	HRR (kW/m^2)	THR (MJ/m^2)	EHC (MJ/kg)
50.0% (H_2SiO_3:GL:EC=1:4:3)+50.0% (MEL:PC=1:20)	8	83	79.1	65.1	4.7	62.8
H_2SiO_3:GL:EC=1:4:3 (4% H_2O)[21]	7	75	86.5	65.6	4.1	53.7
MEL:PC=1:20[22]	6	180	69.8	52.7	12.6	79.5

strated at Figure 3(f), (h). Moreover, open pores are visible at pictures of PUFs obtained from oligoetherols 50.0% (H_2SiO_3: GL:EC=1:4:3) and 50.0% (MEL:PC=1:20) as well as 33.3% (H_2SiO_3: GL:EC=1:4:3) and 66.7% (MEL:PC=1:20) after thermal exposure at 175 °C or higher temperature. The broken and open pores are marked with envelope at Figure 3(e)-(h). Presumably the open pores are responsible for increased water uptake and heat conduction coefficient.

Cone calorimeter tests were performed to study the PUFs flammability. Ignition time is one of the critical parameters for the materials thermal resistance, higher the ignition time, the longer it takes for the material to heat up, ignite, and initiate a fire. According to the performed tests the PUF with 1,3,5-triazine ring obtained from oligoetherol MEL:PC=1:20 ignited after 6 s and the PUF modified with silicon ignited after 7 s, while the PUF obtained both 1,3,5-triazine ring and silicon (obtained here from mixture of oligoetherols) ignited after 8 s (Table 9). Total time of flaming (TTF) was the longest for PUF with 1,3,5-triazine ring (180 s); heat release from the PUF was slow, while TTF was the shortest for PUFs modified only with silicon and obtained from mixture of oligoetherols (75-83 s). Heat release profile from PUFs is presented at Figure 4. The silicon-modified PUFs obtained from mixture of oligoetherols had considerably higher heat release rate (HRR) than PUF obtained from MEL:PC=1:20 oligoetherol. The PUF obtained from oligoetherol H_2SiO_3:GL:EC=1:4:3 reached maximum HRR after 28 s from ignition, while PUF obtained from mixture of oligoetherols reached maximum HRR after 53 s. The silicon-containing PUF flamed fastest, the 1,3,5-triazine based PUF flamed slower, while the slowest flaming was found for PUF based on mixture of oligoetherols. The latter reaches maximum flaming rate after the longest time and slowly releases heat. PUFs modified with silicon or obtained from mixture of oligoetherols have larger values of maximum HRR in comparison with PUFs based on 1,3,5-triazine ring. This is consistent with larger apparent density of silicon-containing PUFs in comparison with that obtained from MEL:PC=1:20 oligoetherol.[21,22] The mass loss of PUFs correlate with apparent density; the higher apparent density, the larger mass loss upon flaming. Thus, the PUF obtained from oligoetherol H_2SiO_3:GL:EC=1:4:3 showed the largest mass loss, equal 86.5%. Effective heat of combustion (EHC) depends on kind of PUF (Table 9). The PUF obtained from MEL:PC=1:20 oligoetherol releases the largest amount of heat (79.5 MJ/kg). The PUF obtained from oligoetherol synthesized from metasilicic acid released less heat (53.7 MJ/kg), while PUF obtained from mixture of oligoetherols indicated intermediate amount of released heat (62.6 MJ/kg). Considering the total heat release (THR), it has been noticed that PUF obtained from mixture of oligoetherols releases comparable amount of heat to silicon-modified PUF but 2.5 times less than PUF based on oligoetherol synthesized only from melamine and PC as substrate. This property of silicon-modified PUFs obtained here might be advantageous.

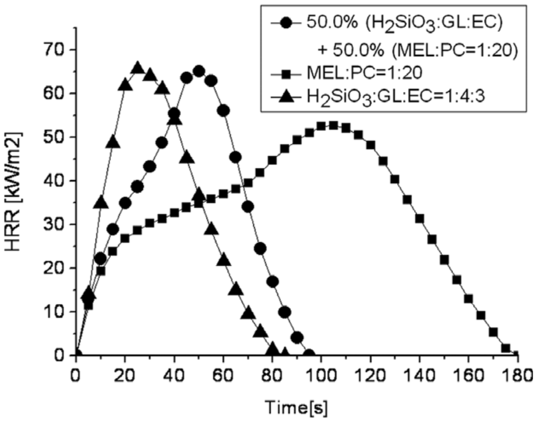


Figure 4. The course of changes in the HRR as a function of time during the combustion of polyurethane foams.

4. Conclusions

1. The PUFs with 1,3,5-triazine ring and silicon were obtained using the mixture of oligoetherols synthesized from melamine, propylene carbonate, metasilicic acid, glycidol, and ethylene carbonate.
2. Obtained PUFs have improved mechanical and thermal resistance in comparison with classic rigid PUFs. Some of PUFs also indicated decreased flaming rate.
3. The increase of 1,3,5-triazine ring percentage in PUF results in increased thermal resistance, while increasing silicon percentage results in mechanical resistance improvement. That provides the possibility to tune thermal properties and mechanical resistance depending on their practical destination, which broadens the applicability of PUFs based on melamine- or metasilicic acid- derived oligoetherols.
4. Long term heating of PUFs at 150-200 °C leads to increase of compression strength and reduction of flammability of annealed PUFs. The PUFs exposed thermally at 150 °C for one month increase their oxygen index up to 23.6%, i.e. they become self-extinguishing. Heating PUFs at 175 °C results in increased oxygen index to 43.0%, rendering the material non-inflammable.

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