

Polyetherols from melamine cyanurate and ethylene carbobate – synthesis and application

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The results of the study on the reactions of melamine cyanurate with ethylene carbonate were presented. As a result of the reactions, polyetherols containing thermostable 1,3,5-triazine and perhyroxo-1,3,5-triazine rings in their structure were obtained. Basic physical properties such as density, viscosity, hydroxyl number, weight changes were measured. The polyetherols were applied as a polyol component to receiving of thermoresistant polyurethane foams. Some of the properties of the obtained foams were investigated. The value of the apparent density is between 51 and 71 kg/m³, compressive strength 222–356 kPa and the content of the open pores between 14–33%. Thermal resistance was also studied by means of the TGA method. It was found that oxygen index of the selected compositions is between 20–22%.

Keywords: melamine cyanurate, ethylene carbonate, polyetherols, polyurethane foams.

INTRODUCTION

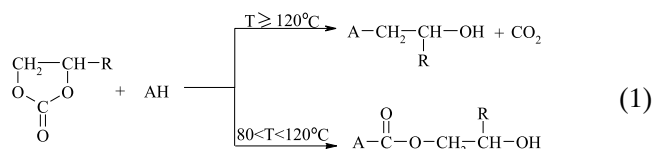
Melamine cyanurate (MC) is successfully applied as an agent increasing thermal resistance of plastics because of the presence of 50% nitrogen and of s-triazine as well as perhydro-1,3,5-triazine rings^{1–4}. An example of plastics for which the increased resistance to thermal degradation is desirable, is polyurethane foam. There are reports in literature^{5,6} concerning the application of powdered MC to obtain polyurethane foams. However, insertion of solid into polyols master batches causes a significant increase of their density, which may cause clogging of the nozzles giving polyol blend. Transfer of MC in the reaction with ethylene carbonate into liquid polyetherols could solve the problem. The polyetherols could be successfully applied as a polyol component to foamed polyurethane plastics. Thermostable s-triazine and perhydro-1,3,5-triazine rings introduced in this way should affect the increase of the thermal resistance of the foams obtained.

Alkylene carbonates (AC) of general formula (I) are cyclic esters of carbonic acid and appropriate vicinal diols:



Such AC as ethylene carbonate and propylene carbonate are excellent solvents of many low molecular compounds as well as polymers because of their polar character⁷. Due to non-toxicity propylene carbonate is used as a solvent of paints, varnishes and plastics⁸. AC are also used as modifiers in the production of solid, fast cross-linking polyurethanes as well as of polyurethane adhesives.

Alkylene carbonates were proved to be also suitable for hydroxyalkylation of azacyclic compounds. The route of the reaction depends on the temperature of the reaction, and kind of the catalyst and the structure of A group:



where:

R = -H, -CH₃.

Reactions accompanied by carbon dioxide evolution usually run at the temperature over 100°C (in the case of amines within the range 140–170°C with or without an alkaline catalyst⁹).

MC is a compound containing active hydrogen atoms, obtained by a direct reaction of melamine with cyanuric acid in an aqueous solution.

This paper presents the synthesis of polyetherols based on MC and ethylene carbonate as a hydroxyalkylating agent as well as the application of the obtained polyetherols to foam polyurethane plastics.

EXPERIMENTAL

Synthesis of Polyetherols

In a 500 cm³ reactor equipped with a mechanical stirrer and reflux condenser, 25.5 g (0.1 mole) melamine isocyanurate, appropriate amount of ethylene carbonate (EC) (158.4 g (1.8 mole); 176 g (2.0 mole); 211.2 g (2.4 mole) or 422.4 g (4.8 mole) and catalyst (1,4-diazabicyclo[2.2.2]octane (DABCO)) (2; 4 or 8 g/mole MC were placed. The reaction mixture was heated to an appropriate temperature (160°C, 165°C or 170°C.). The progress of the reaction was monitored by the IR spectral measurements of aliquots until the band of valence vibrations of ethylene carbonate carbonyl group at 1790 cm⁻¹ disappeared. For the same polyetherols hydroxyl number was determined.

Foam Preparation

Attempts of foaming were carried out in small 500 cm³ test cups at room temperature. To a sample of 10 g of a polyol, 1.5 wt % of surfactant, 0.15–0.47 wt % of triethylamine – catalyst and 2 wt % of water were added. As a polyol component a mixture consisting of polyetherol obtained in the reaction of MC with ethylene carbonate and other polyesterols (Poles 50/23, Poliester 350) or polyetherols (Rokopol D2002, Rokopol G500) was used. As a surfactant PC Stab EP05 was used. After careful

mixing of the components, a pre-weighed amount of 4,4'-diphenylmethane diisocyanate (MDI) was added.

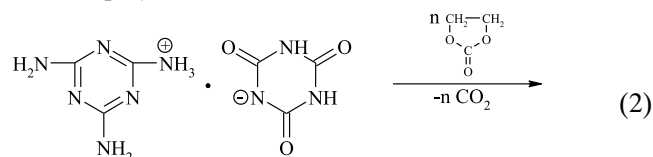
Analytical Methods

The reaction of MC with EC and PC was monitored by the determination of EC. $^1\text{H-NMR}$ and the spectra of the products were recorded with spectrometer NMR Varian Unity Plus 200 MHz in deuterated chloroform (CDCl_3), and hexamethyldisiloxane (HMDS) reference.

Thermal analyses (DTA, DTG, and TG) of polyetherols and polyurethane foams were performed in a ceramic crucible at 20–700°C temperature range, with 100 min registration time, 200 mg sample, under air atmosphere with TGA Q50 V20.8, Bulid 34 derivatograph. The following properties of polyetherols were determined: pycnometer density¹⁰, Höppler viscosity¹¹ and hydroxyl number¹². The following properties of foams were determined: apparent density¹³, compressive strength¹⁴, content of open pores¹⁵, oxygen index¹⁶ (Fire Testing Technology Limited, UK).

Results

From the literature review, concerning physical and chemical properties of alkylene carbonates^{8,9}, the compounds should be good solvents for MC and react with it towards polyetherols formation:



where: $x + y + z + w + p + q + r = n$, $0 < r < 1$, $n = n_0 - n'$,

n – number of moles of ethylene carbonate, which reacted with MC

n_0 – initial number of moles of ethylene carbonate,

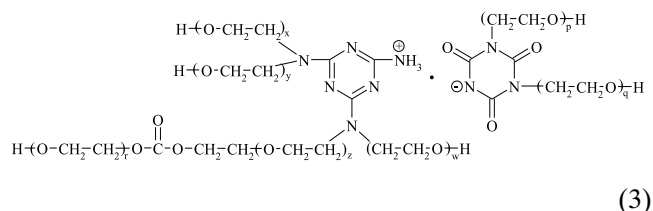
n' – number of moles of ethylene carbonate, which was decomposed

As expected, the reaction proceeded without the solvent. The reaction was carried out with or without the catalyst. As the catalyst 1,4-diazabicyclo-[2.2.2]octane (DABCO) was used. In Table 1 the conditions of the reaction are presented.

It has been stated that MC is very well digested in hot EC giving polyetherols. On the bases of $^1\text{H-NMR}$ spectrum it has been stated that carbonate groups are built in the struc-

ture of the product, however the amount of the groups does not exceed 1 mole/mole of product.

As it follows from the data of Table 1, the product mass, found from mass balance, is less than that one calculated from the initial molar ratio of reagents. This means that in the initial phase of the reaction a part of alkylene carbonate decomposes to the easily volatile ethylene oxide:



From the literature¹⁷, the degree of decomposition depends on the kind of the catalyst used, and on the structure of alkylene carbonate. From the data of table 1, the largest decomposition is for 170°C without a catalyst.

Liquid, dark brown substances similar to resins have been obtained as the result of the synthesis. Some of the properties of the selected polyetherols, such as density, viscosity and hydroxyl number, obtained in the paper are presented in Table 2.

Thermal resistance of polyetherols obtained has been also determined by means of thermo gravimetric analysis. On the plot of TGA analysis of pure MC one endothermic peak derived from s-triazine and perhyroxo-1,3,5-triazine rings, decomposition is observed. A maximum of the peak occurs at 410°C (Fig. 1). In the case of polyetherols two endothermic peaks are observed (Fig. 2). The first one at 262°C, refers to the decomposition of polyetherols chains, and the second one at 383°C to the decomposition of MC ring.

The results presented above indicate that polyetherols obtained in this work are suitable to receive foamed polyurethanes with increased thermal resistance.

If as a polyol component only the polyetherol obtained from MC and EC has been applied, the compositions were too reactive and foam increase took place before reaching an appropriate degree of cremation. The foam obtained was characterized by a low degree of foaming and heterogeneity. In order to lengthen the composition growth time other polyols components were applied. Addition of Poles 50/23 caused a double increase in composition growth time and application of dibutyltin laurate as a catalyst prevented the foam collapsing. Longer times were obtained, when Rokopol

Table 1. The conditions of MC reaction with ethylene carbonate (EC)

Run	Initial molar ratio of MC:EC	Amount of catalyst [g/mole MC]	Temperature [°C]	Reaction time [h]	Time of MC dissolution [min.]	Number of moles of EC decomposed [mole/mole MC]	Effective number of moles of EC reacted
1.	1:18	8	170	7	30	1.4	16.6
2.	1:18	8	160	8	40	0.7	17.3
3.	1:18	4	170	8	25	1.2	16.8
4.	1:18	4	160	8.5	50	1.0	17.0
5.	1:20	–	170	10.5	50	1.4	18.6
6.	1:24	2	160	8	30	0.5	23.5
7.	1:48	2	165	11	20	0.5	47.5

Table 2. The properties of polyetherols obtained from MC and EC

Series	Initial molar ratio MC:EC	Amount of catalyst [g/mole MC]	Temperature [°C]	Density [g/cm ³]	Viscosity [cP]	Hydroxyl value [mg KOH/g]
1.	1:20	–	170	1.05	980	420
2.	1:24	2	160	1.10	1050	380

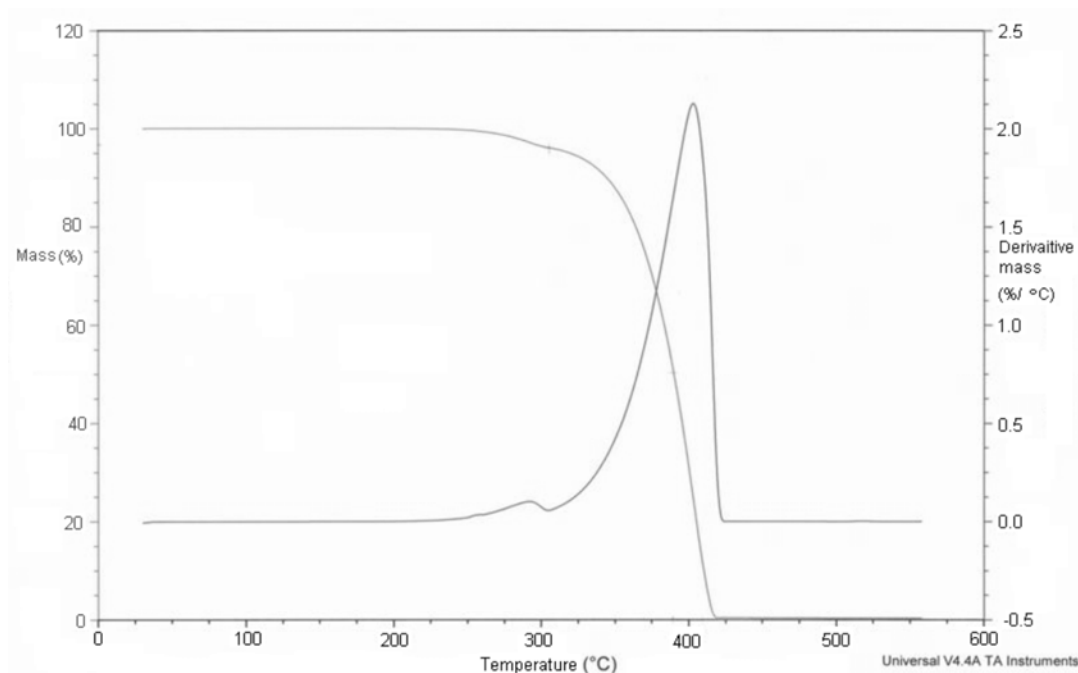


Figure 1. TGA plot of MC

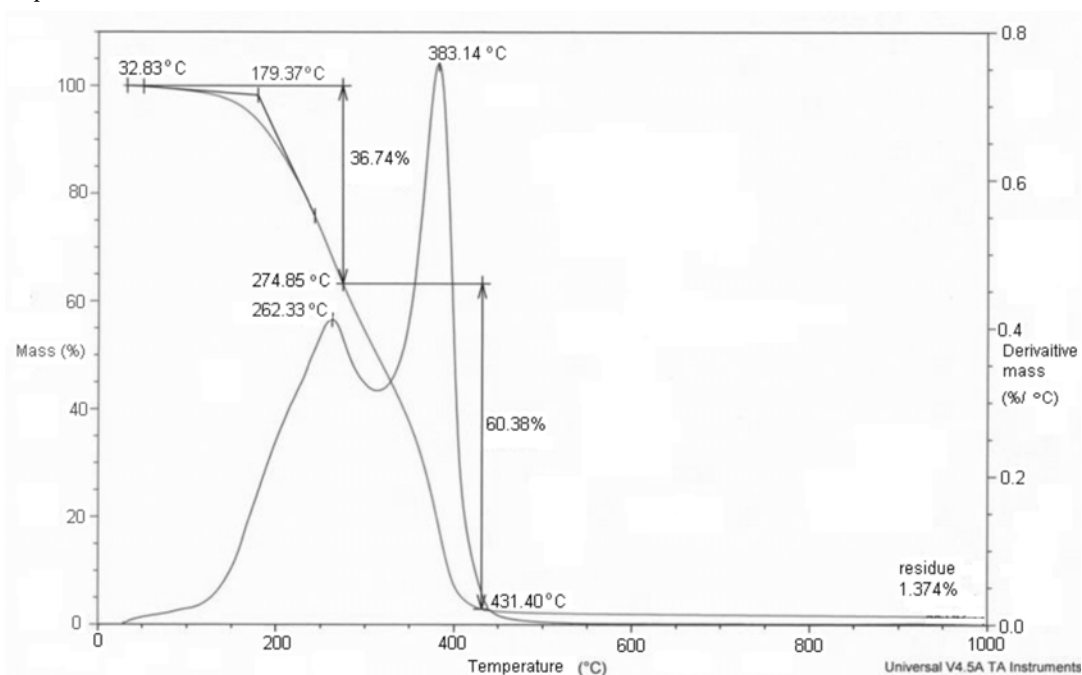


Figure 2. TGA plot of polyetherole obtained from MC and EC

D 2002 were applied, however the amounts greater than 20g/100g polyol mixture caused big polymerization shrinkage of the foam. A good foaming degree was obtained for Rokopol G 500 and Polyester 350 applied as the additions.

Some properties of the selected foams, such as apparent density, compressive strength, (parallel and perpendicular to growing) oxygen index and content of open pores were determined. The results are collected in Table 3.

An apparent density of the foams obtained is within the range 50–100 kg/m³, which classifies them to the rigid or semi-rigid ones. In turn compressive strength falls within the range 220–360 kPa and is characteristic for the rigid foams.

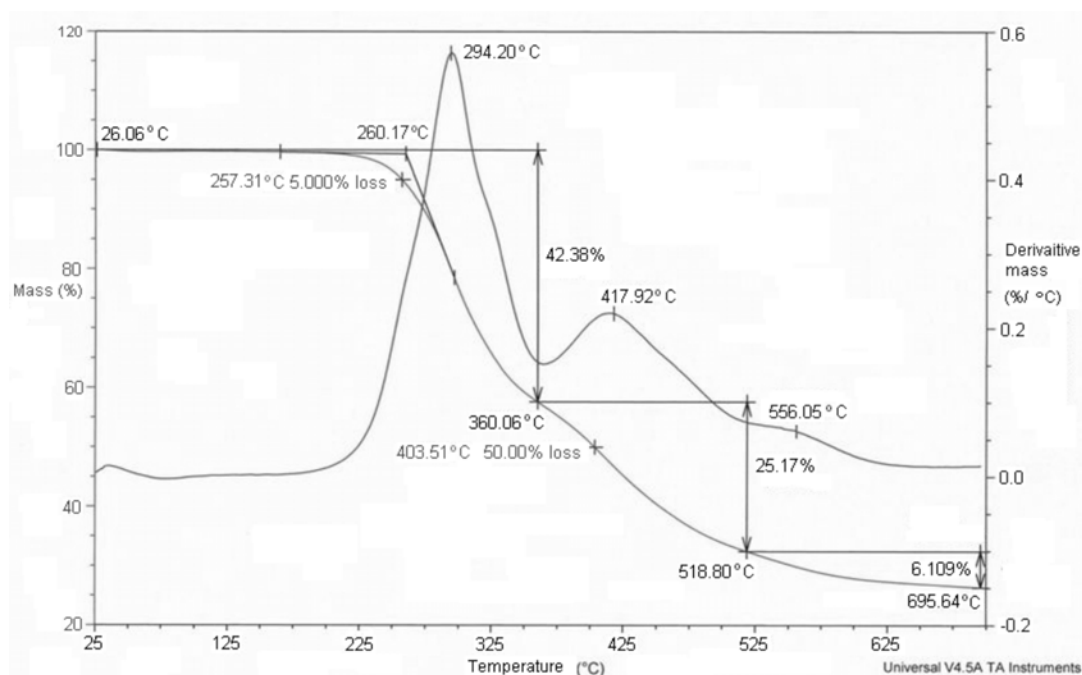
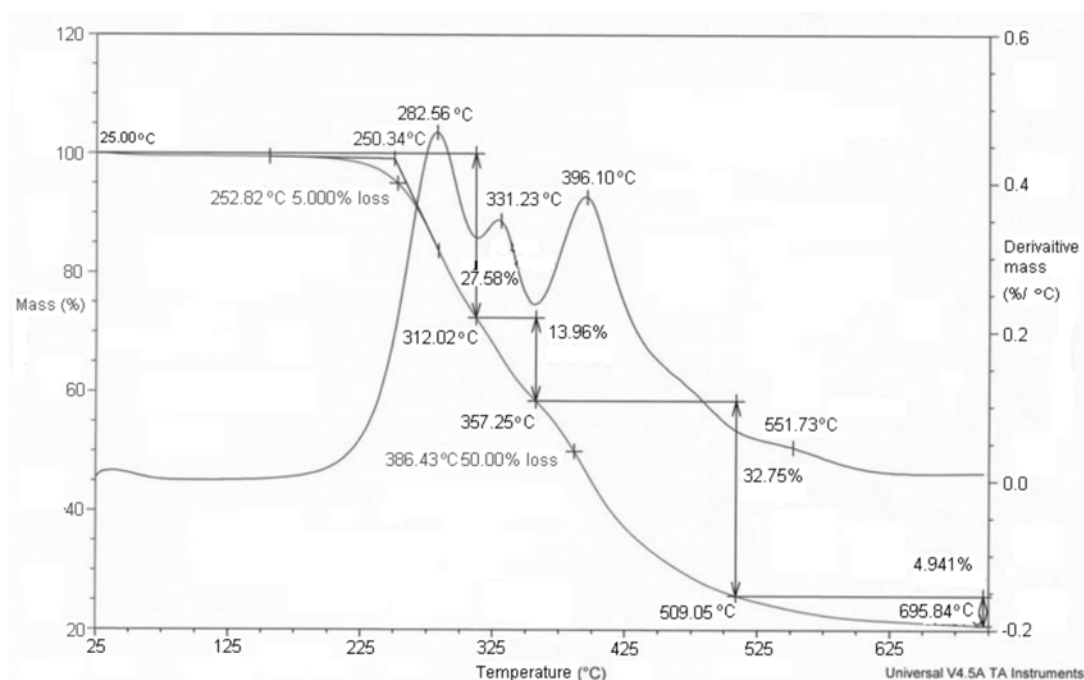
A thermal resistance of the foams has been also examined by the TGA method. In Figures 3,4, additions of other polyesterols or polyetherols to the polyol compositions

obtained from MC do not have a negative impact on the thermal resistance of the obtained foams. In the case of polyurethane foam obtained from polyol mixture, containing an addition of Rokopol D 2002, 50% weight loss takes place at 386°C. In turn, in the case of polyurethane foam obtained with the addition of Polyester 350, 50% weight loss takes place at 403°C.

It is concluded that the introduction of s-triazine and perhydro-1,3,5-triazine rings to the structure of MC causes a significant improvement of thermal resistance of the foams obtained with the participation of polyetherols synthesized from MC and EC, as compared with traditional polyurethane foams, whose thermal resistance is 120°C only.

Table 3. Properties of the selected foams

Run	Polyetherol from MC and EC/ other polyetherol or polyesterol [wt parts/100]	Amount of MDI [g/100 g polyol]	Amount of catalyst [g/100 g polyol]	Apparent density [kg/m ³]	Compressive strenght 10% compression, [kPa] parallel to growing	Compressive strenght 10% compression, [kPa] perpendicular to growing	Oxygen index [%]	Content of open pores [%]
ROKOPOL D 2002								
1.	80/20	112	0.15	63.8	222	196	22.1	19.4
ROKOPOL G 500								
2.	50/50	118	–	51.3	356	274	< 20	15.7
3.	80/20	125	–	54.6	307	271	< 20	14.6
POLYESTER 350								
4.	50/50	123	–	55.4	278	205	21.7	33.2
5.	80/20	126	–	70.9	325	274	21.8	14.4

**Figure 3.** Plot of TGA for the foam obtained from polyol mixture with 50 wt % of POLYESTER 350**Figure 4.** Plot of TGA for the foam obtained from polyol mixture with 20 wt % of ROKOPOL D 2002

CONCLUSIONS

1. MC reacts with EC towards polyetherols containing s-triazine and perhydro-1,3,5-triazine rings in their structure, while carbonate groups are built in the structure of the product, however the amount of the groups does not exceed 1 mole/mole of product.

2. Physical parameters of the obtained polyetherols as well as their thermal analysis indicate that the compounds are suitable to receive foamed polyurethanes with increased thermal resistance.

3. The use of other polyetherols or polyesterols to reduce the reactivity of the synthesized polyetherol caused an extension of the time of composition as well as obtaining more homogeneous foam.

4. The obtained foams are characterized by a much higher thermal resistance than the traditional polyurethane foams.

LITERATURE CITED

1. Casu, A., Camino, G., De Giorgi, M., Flath, D., Morone, V., Zenoni, R., Fire-retardant mechanistic aspects of melamine cyanurate in polyamide copolymer. *Polym. Degrad. Stab.*, 58 (1997), 297–302, DOI:10.1016/S0141-3910(97)00061-X.
2. Roland, W., Reinhard, B., Andreas, D. (2007). EP No. 1731559. European Patent Office.
3. Morival, G., Hervy, C. (1988). US Patent No. 4786673. Washington, D.C.: U.S. Patent and Trademark Office.
4. Kasowski, R., Martens, M. (2000). US Patent No. 3,025,419. Washington, D.C.: U.S. Patent and Trademark Office.
5. Modesti, M., Lorenzetti, A., Simioni, F. and Checchin, M. (2001). Influence of different flame retardants on fire behaviour of modified PIR/PUR polymers. *Polym. Degrad. Stab.* 74(3), 475–479, DOI:10.1016/S0141-3910(01)00171-9.
6. Zatorski, W., Brzozowski, Z. (2003). Pol. Patent No. 198605. Warsaw, Patent Office of The Republic of Poland.
7. Mazo, G.Y., Ross, R.J., Kneller, J.F., Mazo, J. (1999). U.S. Patent No. 5,939,517. Washington, D.C.: U.S. Patent and Trademark Office.
8. Klimiec, J., Fabisz, E., Researches on synthesis of propylene carbonate. *Chem. Ind.* 79 (10) 339–340 2000.
9. Clements, J.H. Reactive Applications of Cyclic Alkylene Carbonates. *Ind. Eng. Chem. Res.* (2003). 42 (4), pp 663–674, DOI: 10.1021/ie020678i.
10. Kowalski, P. (2004). *Laboratory of Organic Chemistry*; WNT: Warsaw, (in Polish).
11. Kocot-Bończak, D. (1977). *Laboratory Experiments in Physical Chemistry* PZWL: Warsaw, (in Polish).
12. Polish Committee for Standardization (1993). Polish Standards: Polyethers for polyurethanes – Test methods-Determination of hydroxyl number. PN-C-89052-03: Method A. Poland.
13. Polish Committee for Standardization (1999). Polish (European) Standards: Products for thermal insulation for building – Determination of apparent density. PN-EN 1602. Poland.
14. Polish Committee for Standardization (1998). Polish (European) Standards: Products for thermal insulation for building – Determination of behavior during compression. PN-EN 826. Poland.
15. Polish Committee for Standardization (2005). Polish Standards: Rigid porous plastics – Determination of percentage volumetric content of open and closed cells. PN-ISO 4590. Poland.
16. Polish Committee for Standardization (2006). Polish (European) Standards: Plastics – Determination of flamma-

bility by oxygen index – Part 2: Test at room temperature. PN-EN ISO 4589-2. Poland.

17. Mc Entire, E.E., Gipson, R.M. (1981). U.S. Patent No. 4 265 821 Washington, D.C.: U.S. Patent and Trademark Office.