

Properties of Rigid Polyurethane-Polyisocyanurate Foams Modified with the Selected Fillers

Bogusław Czupryński, Joanna Paciorek-Sadowska, Joanna Liszkowska

Chair of Chemistry and Technology of Polyurethanes, Kazimierz Wielki University, Bydgoszcz 85-064, Poland

Received 17 April 2008; accepted 1 June 2009

DOI 10.1002/app.30937

Published online 15 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Rigid polyurethane-polyisocyanurate foams (PUR-PIR) containing from 2.5% to 20% w/w of fillers (talc, aluminum hydroxide, chalk, starch and borax) were the subject of our studies; a reference sample was PUR-PIR foam with no filler added. Apparent density, compressive strength, brittleness, content of closed cells, retention (flammability) and softening point of foams were determined and the products were analyzed by thermogravi-

metric method. These parameters were the basis to determine effect of type and participation of the fillers studied on physicochemical, heat, and thermal properties of foams. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2460–2469, 2010

Key words: polyurethane-polyisocyanurate foams; powder fillers; physicochemical; heat and thermal properties

INTRODUCTION

At present, polyurethanes are one of the most rapidly developing branches in technology of polymers. These plastics became a significant item amongst plastics, first of all due to their wide application in rigid, semi-rigid, soft and flexible forms. Their density can be easily adjusted from 12 kg/m³ to 1000 kg/m³, what can not be achieved in the case of none of the known chemical material.¹

Properties of polyurethane can be modified in desirable direction by changing the type of raw material, their mutual quantitative proportion, conditions of processing, apparent density of product and other.^{2,3-8}

Their considerable part is produced in the form of rigid foams destined for insulations in many industrial branches, building engineering, refrigeration, heat engineering, etc. Rigid polyurethane foams are thermo insulating materials whose technical parameters surpass both foamed polystyrene and mineral wool. Thermal conductivity (in W/mK) of rigid PUR foam is within the range from 0.019 to 0.026, while it is from 0.042 to 0.052 for mineral wool and from 0.031 to 0.040 for foamed polystyrene, respectively. Foam of 5 cm in thickness has the same insulating effect as the foamed polystyrene of about 10 cm. Application of rigid polyurethane foams as the heat insulations is restricted by such parameters as heat and thermal resistance and price.^{1,2}

Heat resistance should be distinguished from thermal resistance since these parameters concern two different phenomena. Heat resistance is connected with the physical changes occurring in polyurethane foam 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 foam structure. This phenomenon involves degradation of polymer what is manifested by reduction of molecular weight.⁹⁻¹¹

Thermal resistance of foams is connected mainly with temperature of the thermal dissociation of bonds occurring in rigid polyurethane foams. Urethane bond formed in reaction of aromatic polyisocyanate with aliphatic polyol is characterized by temperature of thermal dissociation about 200°C. Ether or ester bonds (temperature of thermal dissociation about 350°C and 260°C, respectively) are introduced into polyurethane chain with polyol. Application of water in order to obtain porophor (CO₂) results in formation of urea and biuret bonds in the chain of high-molecular compound whose temperatures of dissociation are 250°C and from 130°C to 145°C, respectively. Moreover, isocyanurate and carbimide bonds (temperature of dissociation about 300°C and 240°C, respectively) occur in polyurethane-polyisocyanurate foams.^{1,2}

Studies on heat and thermal resistance of polymers are carried out in many research centers in our country and abroad.¹²⁻¹⁹ From many years, in Chair of Chemistry and Technology of Polyurethanes of

Correspondence to: B. Czupryński (czupr@ukw.edu.pl).

Kazmierz Wielki University in Bydgoszcz (Poland), the studies on improvement of heat and thermal properties of the rigid polyurethane-polyisocyanurate foams have been carried out. Among others, effect of boroorganic compounds (liquids) on these properties of foams was investigated. In the case when boroorganic compounds (liquids) were added to a foam composition, the improvement of heat and thermal properties of foams in comparison to standard foam (without boroorganic compounds added)⁹⁻¹¹ was observed. Boroorganic compounds are terminated with reactive hydroxyl groups which react with components of composition for preparation of foams (polyurethane premix). Borates behave in foam composition as a typical chain extenders of polymer. As the amount of borates is increased in foam composition, the growth of flexible segments occurs, among others, what contributes to increase in heat and thermal resistance.

Rigid polyurethane foam, although it is the best insulating material, is not applied in building industry on a mass scale due to its high price; its price is higher than that of foamed polystyrene or mineral wool. Reduction of foam price becomes possible, among others, by application of fillers for foam preparation. The powder fillers applied to prepare rigid polyurethane foams should fulfill many requirements. They can not deteriorate functional properties of foams. They should easily disperse in polyol premixes and they should not deteriorate conditions of processing. A good filler should be characterized by possibly the lowest sedimentation in suspension and in the case when a sediment is formed, it should be easily intermixed. The fillers should not absorb constituents of composition, particularly catalysts, because reduction of their concentration can result in disturbances of polyaddition.¹

When the costs of PUR-PIR foam production will be reduced, they will be competitive to other materials commonly applied for insulating e.g., foamed polystyrene, mineral wool and other.

The aim of our studies was to determine effect of the selected fillers on physicomachanical properties of the rigid polyurethane-polyisocyanurate foams such as heat and thermal resistance. The foams were prepared with addition of the following powder fillers: talc, borax, aluminum hydroxide, chalk, and starch.

EXPERIMENTAL

Materials

Basic components of foams

The polyether with trade name Rokopol RF-55 (product of oxypropylation of sorbitol $L_{OH} = 490$ mg KOH/g, produced by NZPO "Rokita", Brzeg Dolny, Poland) and Ongromat CR 30-20 (technical polyiso-

cyanate whose main component is diphenylmethane 4,4'-diisocyanate, made in Hungary) were used to prepare the rigid PUR-PIR foams. The density of Ongromat CR 30-20 at temperature of 25°C was 1.23 g/cm³, its viscosity was 200 mPa s. Content of -NCO groups was 31%. Polyether 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 (triethyleneamine produced by Hüls, Germany) in the form of 33% solution in dipropylene glycol were applied as catalysts in the foam composition. The polysiloxanepolyoxyallyleneoxydimethylene surface-active agent "Sillicone L-6900" (Witco, Sweden) was used as a stabilizer of the foam structure.

The porophor was carbon dioxide formed in reaction of water with isocyanate groups. Moreover, a liquid anti-flammability agent tri(2-chloro-1-methyl-ethyl) phosphate ("Antiblaze TMPC", Albright and Wilson, United Kingdom) was a constant component of foam composition.

Fillers

The powder fillers characterized by properties stated by manufacturers were applied as follows:

- Potato starch, analytically pure, prod. POCh. (Poland), pH of 2% solution at temp. of 25°C 4.5-6.0, glassy temperature $T_g = 152^\circ\text{C}$;
- talc [$\text{Mg}_3(\text{OH})_2\text{Si}_4\text{O}_{10}$, basic magnesium silicate], white powder, prod. Luzenac Naintsch, Germany, density 2.58-2.83 g/cm³ (anti-flammability diluent);
- aluminum hydroxide, prod. Reachim, Russia, white solid, odorless, pH 8-9 (100 g/dm³ H₂O, temp. 20°C), density 2.4 g/cm³, bulk density ~600 kg/m³ (antiflammability diluent);
- chalk (CaCO₃) "Socal N25," prod. Eben Seer Solvay-Werke, Austria, white solid, odorless, powder mineral filler (antipirene reduces flammability and impact of flame);
- borax [$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$, decahydrous sodium tetraborate], Czech production, colorless, weathering in air, slightly soluble in water (at temp. of 21°C 2.7 g/100 cm³) crystalline solid, density at temp. of 20°C 980 kg/m³ (antipirine).

Fillers were dried for 4 h in a drier at temp. from 80°C to 100°C.

Method of preparation of rigid PUR-PIR foams

The foams were prepared in laboratory scale by one-stage method from two-component system (A and

B) at the equivalent proportion of —NCO to —OH groups equal to 3 : 1. Component A was obtained by a precise mixing (speed of stirrer, 1800 rpm; time, 10 s) of the respective amounts of Rokopol RF-55, fillers, catalysts, flame retardant, surface-active agent and water. Component B was Ongromat CR 30-20. Both components (A and B) were mixed (1800 rpm, 10 s) at respective weight ratios and poured onto a rectangular tray (dimensions $195 \times 195 \times 240$ mm). After foaming, the prepared foams were removed from the tray, thermostated for 4 h at temperature of 120°C , seasoned for 48 h at temp. of $20 \pm 4^\circ\text{C}$, cut by band-saw and then, heat and thermal resistances were determined according to the obligatory standards.

METHODS

Determination of foam formation parameters

Process of foam formation was monitored by measurement of times of its consecutive stages. The following times were measured during process of foaming: start time, time of expansion, time of gelation, and time of bounding.

Start time was measured by stop-watch from the moment of confluence of both components to the beginning of foam expansion.

Time of expansion was measured from the moment when the components were mixed to the moment when expansion of foam was finished.

Time of gelation was measured from the moment of confluence of both components to the moment when the free surface of foam ceases to glue to a clean glass rod.

Time of bounding was determined as a time measured from the moment when components were mixed to the moment when a foam obtained mechanical resistance allowing to empty the form freely without deformation of the foam formed.

Determination of physicochemical properties of polyurethane-polyisocyanurate foams

Physicochemical properties of the PUR-PIR foams were determined according to standards accepted for rigid polyurethane foams.

Determination of apparent density

Apparent density of foams was determined according to ISO 845-1988 standard; tests were carried out on 3 cubical samples of each foam in the form of rectangular cubes (volume of 125 cm^3). Samples of foams were measured by slide caliper with accuracy to 0.1 mm and were weighted accurate to 0.0001 g.

Arithmetic mean from densities calculated as mass to volume ratio was accepted as the result.

Determination of compressive strength at sample deformation by 10%

Compressive strength was determined according to standard ISO 844 : 1993, PN-EN ISO 604. Tests were carried out on 5 samples of foam (dimensions $50 \times 50 \times 50\text{ mm}^3$). 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 five measurements was a result.

Determination of brittleness

Brittleness of foams was determined according ASTM C-421-61 standard in an oaken box (dimensions: $190 \times 197 \times 197\text{ mm}^3$) rotating around its axis with a speed of 60 rpm. The box was filled with 24 oak cubes ($20 \times 20 \times 20\text{ mm}^3$). Brittleness was calculated as a loss in mass (in percents) of 12 foam cubes (side of 25 mm) during drum rotation for 10 min in relation to their initial mass.

Determination of foam flammability according to the simplified Butler's chimney test (ASTM d 1692-59T)

Three samples of foams ($150 \times 20 \times 20\text{ mm}^3$) were tested. Combustion was performed in vertical column (chimney) of $300 \times 57 \times 54\text{ mm}^3$ by a flame from gas burner supplied with propane-butane. A flame from the burner was brought into contact with the weighted sample for 10 s; then, the burner was removed and time of the sample free burning was measured by stopwatch. After burning, the samples were weighted again. Time of free burning and retention in chimney test were accepted as a result. Residue of sample mass after combustion (retention in %) was calculated from the formula:

$$R = m_2 m_1^{-1} \times 100$$

where:

- R = retention (residual mass after burning) in %,
- m_1 = mass of sample before burning in g,
- m_2 = mass of sample after burning in g.

Determination of flammability according to horizontal test

Investigations were carried out on three samples of foam ($150 \times 50 \times 13\text{ mm}^3$) according to ASTM D-

1692-74 standard. Samples in horizontal position with the marked line in the distance of 125 mm were set on fire by the flame of propane-butane burner for 60 s. Then, the burner was removed and time of free burning of foam was measured by a stopwatch. Rate of combustion (mm/s) in horizontal test was accepted as a result.

Determination of changes in linear dimensions and volume (ISO 1923 : 1981)

Determinations were performed for three samples of each foam ($50 \times 50 \times 50 \text{ mm}^3$) with the marked direction of expansion. Changes in linear dimensions and volume were determined after 48 h of thermostating at temperature of 120°C . Change in linear dimensions was determined longwise a direction of the foam expansion and it was calculated in % from the formula:

$$\Delta l = \frac{l - l_0}{l_0} \times 100$$

where:

l_0 = length of sample before thermostating,

l = length of sample after thermostating.

However, change in volume of foam was calculated (in %) from the formula:

$$\Delta V = \frac{V - V_0}{V_0} \times 100$$

where:

V_0 = volume of sample before thermostating,

V = 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.

Determination of loss in mass (PN-ISO 4590 : 1994)

Loss in mass was determined for three samples ($50 \times 50 \times 50 \text{ mm}^3$) after 48 h 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:

$$\Delta m = \frac{m_0 - m}{m_0} \times 100$$

where:

m_0 = mass of sample before thermostating,

m = mass of sample after thermostating.

Determination of softening point

Softening point was determined as a thermal resistance under compressive stress according to DIN

53,424 standard. Samples of foam ($20 \times 20 \times 20 \text{ mm}^3$) were subjected to the action of compressive load of 0.25 kg/cm^2 longwise a direction of the foam expansion. 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.

Determination of heat and thermal resistance

Rigid polyurethane-polyisocyanurate 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 within the range of temperature from 20°C to 800°C . Tests were carried out using derivatograph produced by MOM Budapest (Paulik-Paulik-Erdey).

Heat resistance was defined by the determination of softening point by Vicat method (Vicat apparatus, PN-93/C-89024; ISO 306:1987 standards).

IR analysis—determination of heat conductivity and content of closed cells

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)

Heat conductivity was determined by the use of "FOX 200" apparatus (Lasercomp).

Content of closed cells was determined according to PN-ISO 4590 : 1994 standard.

RESULTS AND DISCUSSION

Composition of the reaction mixtures consisted of the constant amounts of the following components: "Rokopol RF-55," 60 g; "Ongromat 20-30," 284 g; Silicone L-6900, 5.16 g; "DABCO 33LV," 3.1 g; catalyst 12, 7.2 g; Antiblaze TMCP, 51.6 g; and distilled water, 3.78 g (Table I). However, the amounts of fillers were different and they were equal to 2.5% w/w (8.6 g), 5% w/w (17.2 g), 7.5% w/w (25.8 g), 10% w/w (34.4 g), 12.5% w/w (43.0 g), 15% w/w (51.6 g), 17.5% w/w (60.2), and 20% w/w (68.8 g) in each case. Content of fillers in foams (in percent) was calculated with respect to the sum of masses of polyisocyanate and polyol applied.

The foams prepared were characterized by the start times from 15 s (standard foam) to 22 s (foam with 20% w/w of chalk added) and times of expanding and gelation were up to 92 s.

Introduction of fillers into the foam composition in amount from 2.5% w/w to 20% w/w/ resulted in

TABLE I
Compositions of Rigid PUR-PIR Foams

Raw materials	Unit	No. of foam									
		0 (standard)	1, 9, 17, 25, 33	2, 10, 18, 26, 34	3, 11, 19, 27, 35	4, 12, 20, 28, 36	5, 13, 21, 29, 37	6, 14, 22, 30, 38	7, 15, 23, 31, 39	8, 16, 24, 32, 40	
Rokpol RF-55	grams	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	
Talc	% w/w	–	2.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0	
Aluminum hydroxide	% w/w	–	2.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0	
Chalk	% w/w	–	2.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0	
Starch	% w/w	–	2.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0	
Borax	% w/w	–	2.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0	
Silicone	% w/w	–	5.16	5.16	5.16	5.16	5.16	5.16	5.16	5.16	
DABCO 33LV	grams	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	
VCatalyst 12	grams	7.2	7.2	7.2	7.2	7.2	7.2	7.2	7.2	7.2	
Antiblaze TMCP	grams	51.6	51.6	51.6	51.6	51.6	51.6	51.6	51.6	51.6	
Distilled water	grams	3.78	3.78	3.78	3.78	3.78	3.78	3.78	3.78	3.78	
Ongromat 20–30	grams	284.0	284.0	284.0	284.0	284.0	284.0	284.0	284.0	284.0	

% w/w in relation to the sum of Rokpol RF 55 and Ongromat 20–30 masses.

change in apparent density of the foams prepared (Fig. 1). Apparent density of standard foam was 37.0 kg/m³. Increase in that value occurred in the cases when chalk (up to 51.2 kg/m³, foam no. 24), aluminum hydroxide (up to 50.9 kg/m³, foam no. 16) or talc (up to 50.1 kg/m³, foam no. 8) were introduced into the foam composition. However, decrease was observed in foams with addition of starch (up to 30 kg/m³, foam no. 32), and borax (up to 15.2 kg/m³, foam no. 40). It proves about a distinct effect of fillers on processes of foaming and in consequence, on favorable (talc, aluminum hydroxide, chalk) and unfavorable (starch, borax) changes in some properties of the modified foams.

As the amount of aluminum hydroxide and talk in foam composition was increased, the increase in compressive strength was observed from 221.7 kPa (foam no. 0, standard foam) to 359.8 kPa (foam no.

16) and 330.0 kPa (foam no. 8), respectively. It was found that in the case of foams containing chalk, starch and borax, the compressive strength was reduced (Fig. 2). The highest decrease was observed in foams with 20% of borax (foam no. 40) added. Increase in compressive strength is connected with increase in apparent density of the foams prepared (foams with talc and aluminum hydroxide). An exception is the foam containing chalk, in which apparent density increases and in spite of that, compressive strength decreases. Increase in apparent density and simultaneously compressive strength results from strengthening of cell structure of foam by filler additives.

Decrease in brittleness of rigid PUR-PIR foams in comparison with the standard foam (foam no. 0, 41.1%) occurred in the case of foams containing talc (foam no. 8, to 18%), aluminum hydroxide (foam no. 16, to 26.6%), starch (foam no. 32, to 9.5%), and

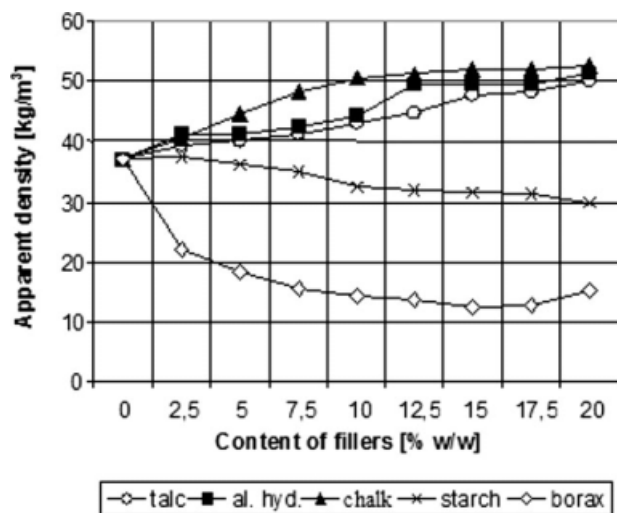


Figure 1 Dependence between apparent density and contents of fillers in foams.

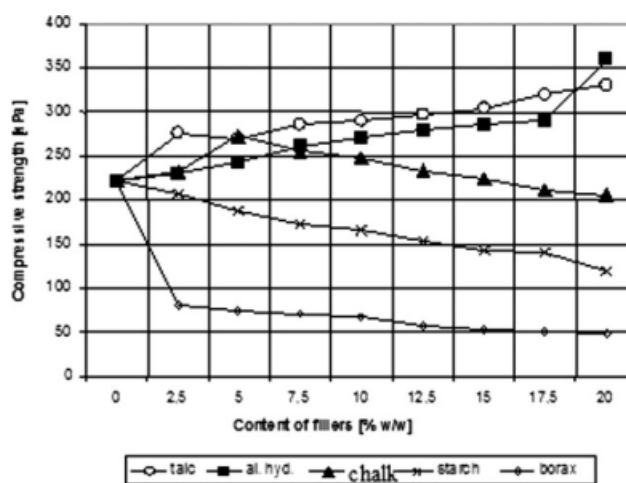


Figure 2 Dependence between compressive strength and contents of fillers in foams.

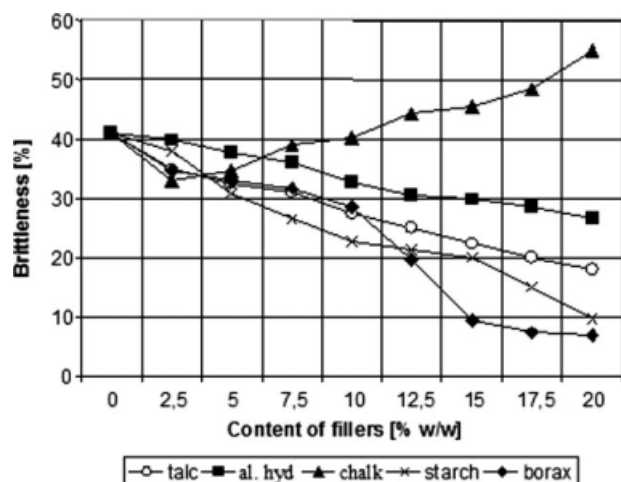


Figure 3 Dependence between brittleness and contents of fillers in foams.

borax (foam no. 40, to 6.9%). Increase in brittleness to 54.8% (foam no. 24) was observed in foams containing chalk (Fig. 3).

As the amount of talc and chalk increased in foam composition from 5% to 20% w/w, the content of the free cells slightly increased to 98.1% (foam no. 8) and to 94.6% (foam no. 24). Decrease in content of the closed cells to 63.8% was observed when borax in amount of 20% w/w (foam no. 32) was introduced into foam composition. Presence of aluminum hydroxide and starch in foams had a slight effect on content of the closed cells in foams (Fig. 4).

Retention (residue after combustion of foams, in percent) for the standard foam was equal to 76.6% (Fig. 5). Retention increased as the amounts of talc, aluminum hydroxide, chalk, and starch were increased in foam composition from 5% to 20% w/w. It reached the value of 95.4% (foam no. 16) in the case of foams with aluminum hydroxide. Retention decreased to 60.0% in foams containing 20% w/w of

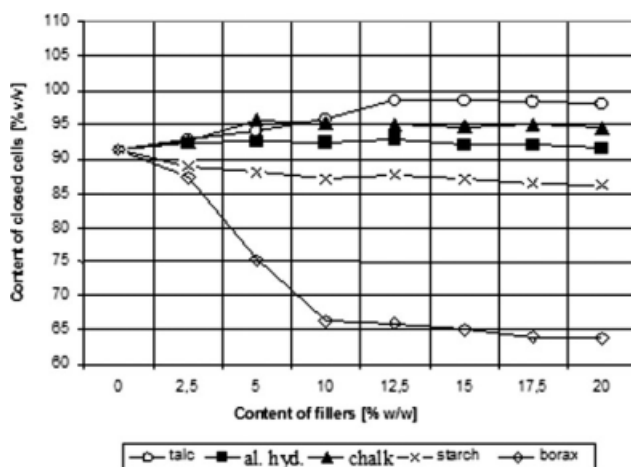


Figure 4 Dependence between content of closed cells and contents of fillers in foam.

borax (foam no. 32). Probably, the partial decomposition of aluminum hydroxide to water and aluminum oxide III causes that liberated water vapor gets into the of burning zone what results in lower concentration of combustible gases and reduction of flame temperature. Moreover, aluminum oxide III forms a protective film on the foam surface and therefore, transportation of volatile combustion products to a flame becomes difficult. Moreover, it attenuates formation of smoke.

Time of foam burning in the chimney test was within the range from 4 to 0 s. for all the foams studied. All foams prepared were self-extinguishing.

Combustion rate (in mm/s) for the standard foam was 9 s. In the case of foams with aluminum hydroxide or chalk added, it decreased to about 0.5 mm/s (foams nos. 9–16 and 17–24).

Insignificant changes in linear dimensions and loss in mass during thermostating of rigid PUR-PIR foams for 48 h at temperature of 120°C were observed. Loss in mass and change in linear dimensions are independent of the content of fillers in foam composition.

As the amount of borax and starch was increased in foam composition, the volume of the foams increased. Foam with 20% w/w of borax increased its volume by about 18% and with 20% of starch by about 7%.

Pores of the foams prepared were characterized by the equal size, what proved, among others, about appropriate selection of surfactant and porophor since they had no effect on the size and shape of pores in foams.

An example of thermogram of foam sample is presented in Figure 6. On the basis of TG (change in mass) and DTG (derivative of change in mass) curves, the following characteristic values have been determined¹²: temperature of the beginning of

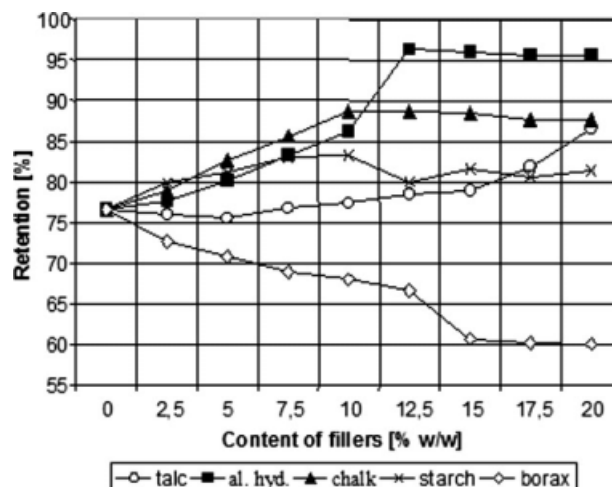


Figure 5 Dependence between retention and contents of fillers in foams.

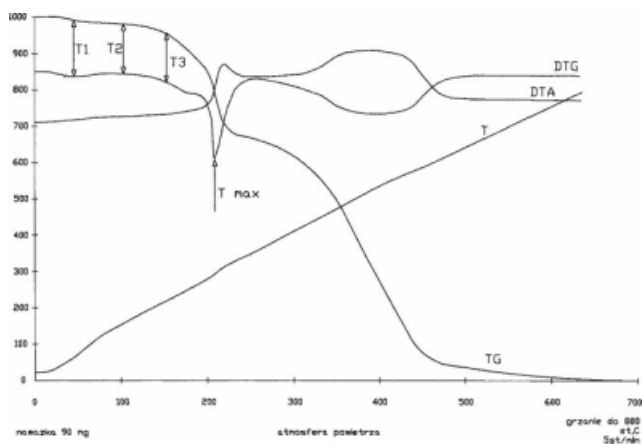


Figure 6 Example of thermogram of polyurethane-polyisocyanurate foam.

change in mass (T_1 , °C), temperature of the beginning of decomposition (T_2 , °C), temperature of the beginning of quick decomposition (T_3 , °C, determined according to ISO 7111 standard as a point of intersection of tangents) and temperature of the highest rate of loss in foam mass (T_{max} , °C, corresponding to extreme on DTG curve).

The first loss in standard foam mass (temperature of the beginning of change in mass) occurred at temperature of 85°C, Figure 7. As the amount of fillers (talc, aluminum hydroxide, chalk, starch, and borax) was increased from 2.5% to 20% w/w in relation to the sum of polyisocyanate and polyol, this temperature increased to 94°C for foam with 20% of talc added, it was almost unchanged for foams with aluminum hydroxide and it decreased to 75°C, 72°C, and do 65°C for foams with chalk, starch and borax, respectively.

The first loss in mass was probably caused by deceleration (diffusion) of carbon dioxide from foam,

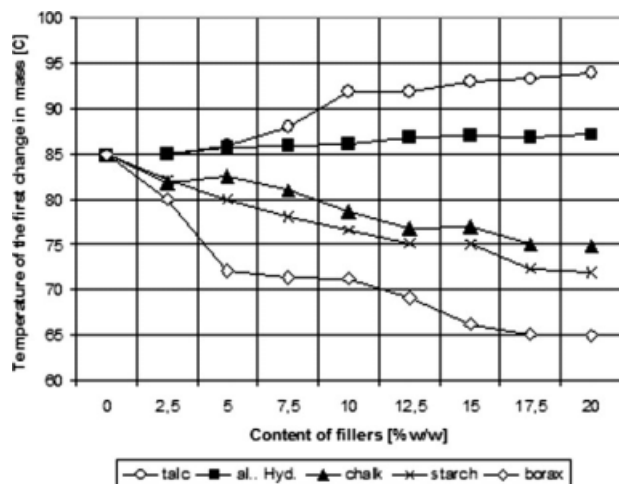


Figure 7 Dependence between temperature of the first change in mass and contents of fillers in foams.

which plays a role of porophor in the foams tested. Carbon dioxide is formed during foam preparation as a result of reaction between the excess of isocyanate groups and water. At temperatures from 85°C to 110°C, diffusion of triethylenamine (DABCO) from foams can occur. Triethylenamine (33% solution in dipropylene glycol) is applied as catalyst of reaction between polyisocyanates and polyols.

Temperature of the beginning of the standard foam decomposition was 210°C, Figure 8. Introduction of talc, aluminum hydroxide, chalk, starch, and borax into the foam composition had effect on temperature of the beginning of rigid foam decomposition. As the amount of fillers was increased in foams from 2.5% to 20% w/w, temperature of the beginning of rigid foam decomposition increased in the case of foams with talc and aluminum hydroxide to 223°C (foam with 20% of talc) and 212°C (foam with 20% of aluminum hydroxide), respectively. However, it decreased in the case of foams prepared with addition of chalk, starch and borax. For foams containing 20% of these fillers, it was 199°C (chalk), 194°C (starch), and 187°C (borax).

Temperature of the beginning of quick decomposition of standard foam was 240°C, Figure 9. As the amount of fillers in foam composition was increased from 2.5% to 20% w/w, this temperature increased from 240°C (standard foam) to 254°C (foams with talc added). For foams with aluminum hydroxide, increase in this temperature was minimal and it was 242°C in the case when 20% of this filler was added. For rigid foams containing chalk, starch and borax, decrease in this temperature to 224°C (foam with 20% of chalk), 216°C (foam with 20% of starch) and 214°C (foam with 20% of borax) was observed.

Among others, temperature of the beginning of quick decomposition of foams is probably due to the

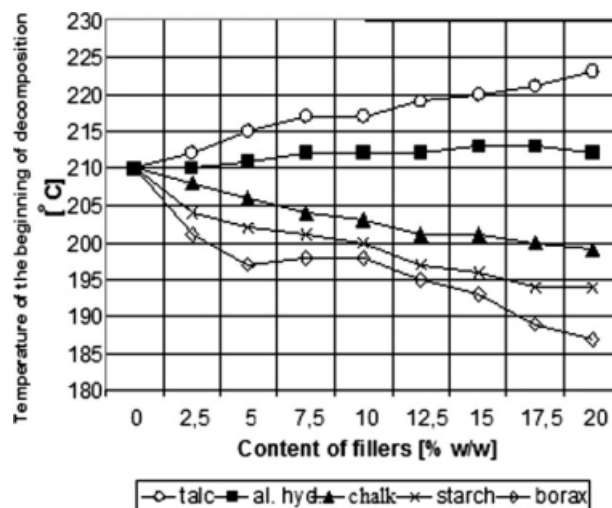


Figure 8 Dependence between temperature of the beginning of decomposition and contents of fillers in foams.

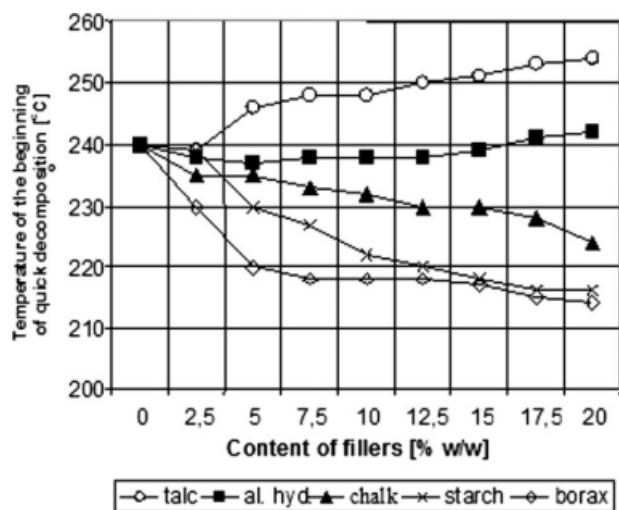


Figure 9 Dependence between temperature of the beginning of the fast decomposition and contents of fillers in foams.

decomposition of urea formed in reaction of polyisocyanate with water, urea groups and biuret bond.

Temperature of decomposition corresponding to extreme on DTG curve for standard foam was 280°C, Figure 10. As the amount of fillers was increased in foam composition from 2.5% to 20% w/w, this temperature increased to 298°C in the case of talc addition (20% w/w). However, it decreased to 270°C (20% w/w of chalk), 260°C (20% w/w of starch), 253°C (20% w/w of borax), respectively. Introduction of aluminum hydroxide into the foam composition had no effect on the above temperature.

Dependence between softening point and content of fillers in foams is presented in Figure 11. Softening point of standard foam was 230°C. The highest increase in this temperature i.e., to 246°C was

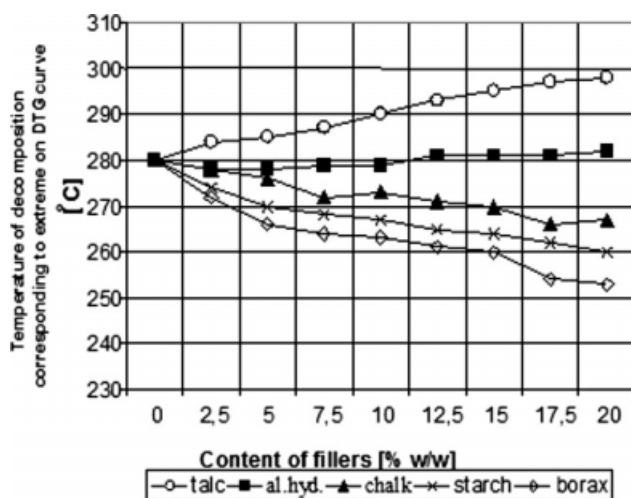


Figure 10 Dependence between temperature of the decomposition corresponding to extreme on DTG curve and contents of fillers in foams.

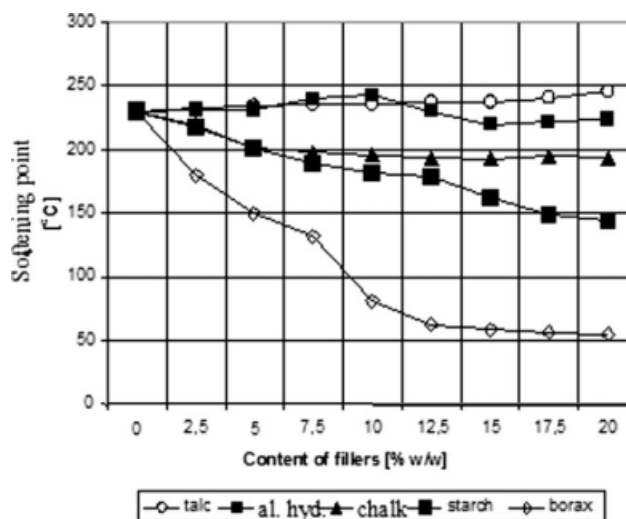


Figure 11 Dependence between softening point and contents of fillers in foams.

achieved as the amount of talc was increased from 2.5% to 20% w/w in foam composition. Introduction of aluminum hydroxide, chalk, starch and borax into the foam composition resulted in decrease of softening point to: 224°C, 194°C, 145°C and 55°C, respectively.

The powder fillers used in our studies i.e., talc, chalk and borax behave in foam composition as the typical unreactive fillers. They do not react with components of recipe for preparation of PUR-PIR foams. After introducing them into premix, stiffening of foam structure occurs. The fillers locate in their skeleton structure Figures 12 and 13. In consequence, a slight increase (talc) or decrease (chalk, borax) in their heat and thermal resistance is observed in comparison with standard foam (with no fillers added). Heat and thermal resistance was practically unchanged in comparison with standard foam as the

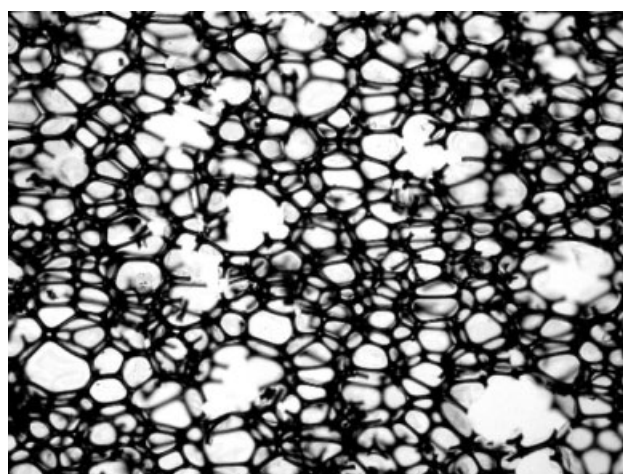


Figure 12 Structure of standard foam (without power fillers added) (Microscope Eclipse 400 E POL, Canon, Japan).

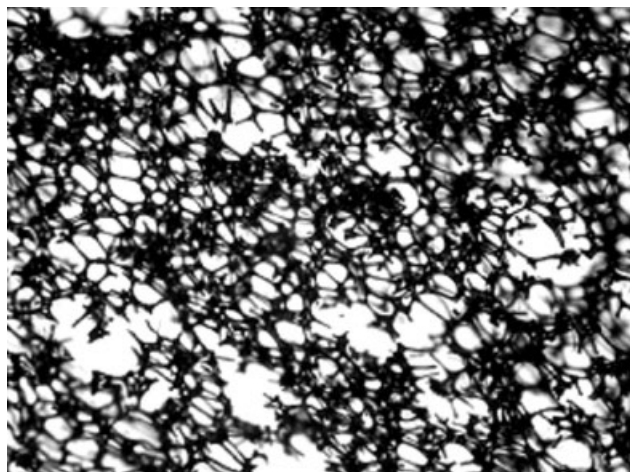
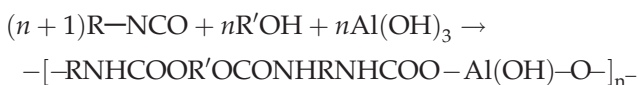


Figure 13 Structure of talc additive in amount of 15% w/w with sum of polyol and polyisocyanate masses (Microscope Eclipse 400 E POL, Canon Japan).

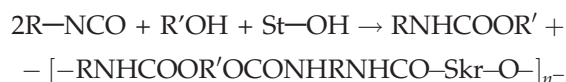
amount of aluminum hydroxide was increased from 2.5% to 20% w/w.

Aluminum hydroxide and starch can be treated as reactive fillers since these compounds contain reactive hydroxyl groups. Regular structure of foams prepared with aluminum hydroxide and starch can prove that these fillers reacted with components of the foam composition. Aluminum hydroxide has three active hydroxyl groups which probably incorporate into the foam structure according to the following reaction:



Polyurethane with incorporated aluminum hydroxide

Starch behaves in foam composition similarly to aluminum hydroxide. Starch contains amylose and amylopectin molecules. Probably, polyurethane with incorporated starch molecule is obtained as a result of reaction of polyisocyanate, polyol and starch.



IR analysis (Fig. 14.) of rigid PUR-PIR foams showed presence of bands characteristic for isocyanurate bond (1710 cm^{-1} – 1690 cm^{-1} and 1410 cm^{-1}), urethane bond (1740 cm^{-1} – 1700 cm^{-1}) and other.

Independently of the kind of filler used, heat conductivity of the foams studied was within a narrow range from 33.5 to 35.5 mW/mK.

SUMMARY

It was found that introduction of the following fillers: talc, aluminum hydroxide, chalk, starch, and borax into the PUR-PIR foam composition had an effect on physicochemical properties of foams including heat and thermal resistance. Addition of talc and aluminum hydroxide into the foam composition in amount from 2.5% to 20% w/w in relation to standard foam (with no filler added) improves their functional properties. Increase in apparent density, compressive strength, and content of closed cells was observed. Brittleness and flammability

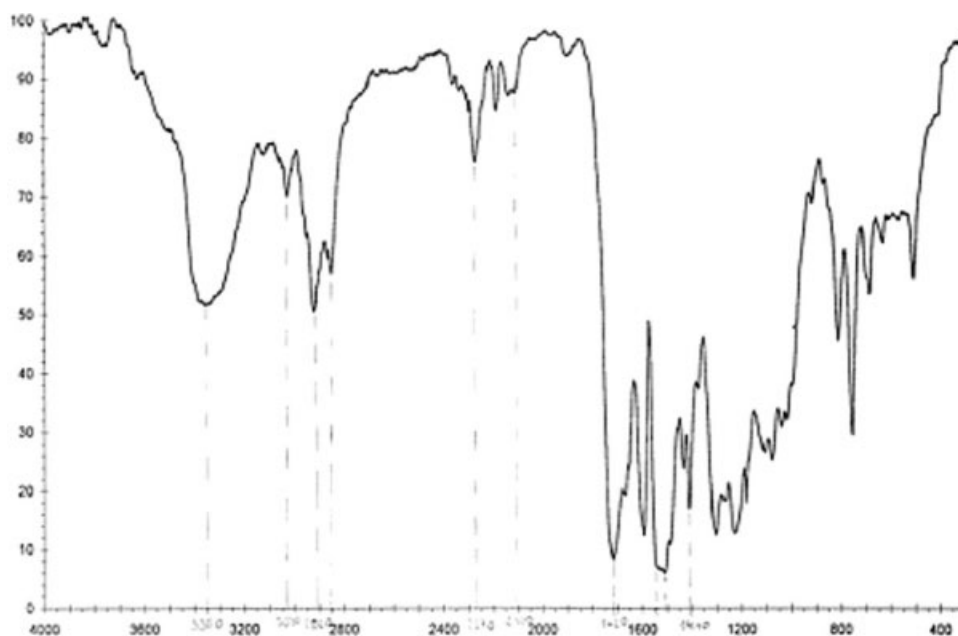


Figure 14 IR spectrum of standard PUR-PIR foam.

of these foams were reduced (increase in retention). In the case when talc was introduced into foam composition, it was found that the parameters increased as follows: softening point from 230°C to 246°C, temperature of the beginning of change in foam mass from 85°C to 94°C, temperature of the beginning of decomposition from 210°C to 223°C, temperature of the beginning of quick decomposition from 240°C to 254°C and temperature of decomposition corresponding to the extreme on DTG curve from 280°C to 298°C.

Rigid polyurethane-polyisocyanurate foams with addition of talc and aluminum hydroxide can find industrial application e.g., in building and heat engineering, etc.

References

1. Czupryński, B. *Zagadnienia z Chemii i Technologii Poliuretanów*; Akademia Bydgoska: Bydgoszcz, 2004; pp 203–204.
2. Uhlig, K. *Discovering Polyurethanes*; Carl Hanser Verlag: Munich, 1999.
3. Brzozowski, Z. K.; Pietruszka, N.; Żabski, L. *Polimery* 2000, 44, 421.
4. Pietruszka, N.; Brzozowski, Z. K. *Polimery* 2000, 45, 282.
5. Pietruszka, N.; Brzozowski, Z. K. *Polimery* 2000, 46, 187.
6. Czupryński, B. *Polimery* 1994, 39, 677.
7. Brzozowski, Z.; Szymańska, E.; Kijańska, D.; Pietruszka, N. *Polym Plast Technol Eng* 1998, 37, 437.
8. Paciorek-Sadowska, J.; Czupryński, B.; Liszkowska, J. *Polimery* 2007, 52, 461.
9. Czupryński, B.; Liszkowska, J.; Paciorek-Sadowska, J. *J Appl Polimer Sci* 2005, 95, 400.
10. Czupryński, B.; Liszkowska, J.; Paciorek-Sadowska, J. *J Polym Eng* 2006, 26, 589.
11. Czupryński, B.; Paciorek-Sadowska, J.; Liszkowska, J. *Chin J Chem* 2006, 24, 1796.
12. Penczek, P.; Rudnik, E.; Arczewska, B.; Ostrowski, R. *Polimery* 1995, 40, 454.
13. Zarzycka-Niemiec, I.; Lubczak, J. *Polimery* 2006, 51, 305.
14. Świerż-Motysia, B.; Pielichowski, K. *Polimery* 2005, 50, 601.
15. Tang, Z.; Maroto-Valer, M. M.; Andrésen, J. M.; Miller, J. W.; Listemann, M. L.; McDaniel, P. L.; Morita, D. K.; Furlan, W. R. *Polymer* 2003, 43, 6471.
16. Datta, J.; Rohn, M. *J Therm Anal Cal* 2007, 88, 437.
17. Kulesza, K.; Pielichowski, K.; Kowalski, Z. *J Therm Anal Cal* 2006, 88, 475.
18. Duquesne, S.; Delobel, R.; Le Bras, M.; Camino, G. *Polym Degrad Stab* 2001, 74, 493.
19. Kulesza, K.; Pielichowski, K. *J Anal Appl Pyrolysis* 2006, 76, 249.