

WOJCIECH ZATORSKI<sup>1\*)</sup>, ZBIGNIEW K. BRZOZOWSKI<sup>1)</sup>, KRZYSZTOF ŁEBEK<sup>2)</sup>

## Production of PUR and PUR-PIR foams with red phosphorus as a flame retardant

### RAPID COMMUNICATION

**Summary** — Two kinds of foams: polyurethane (PUR) and polyurethane-polyisocyanurate (PUR-PIR) ones with red phosphorus as a flame retardant were prepared. As a blowing agent ozone friendly n-pentane with small amount of water was applied. The PUR-PIR foams showed better fire-resistance in comparison with PUR foams without deterioration of functional properties. Effect of synergism in lowering of flammability was obtained *via* the use of two chemical structures inhibiting the flammability: red phosphorus and isocyanurate rings.

**Key words:** polyurethane foam, polyurethane-polyisocyanurate foam, flame retardant, slow-burning polymers, red phosphorus, oxygen index.

The main goals of carrying out research experiments were to form modified polyurethane foams with good fire properties. So far, the use of rigid polyurethane foams is limited by their high flammability. Any solution of these problems will increase their applications in the industry where strict standards of flammability are required. Polyurethane foams is the most efficient insulating material. Any attempt to reduce heat conduction by further reduction of density will cause a rise in radiation transfer. Thermal conductivity of polyurethane foam is about 0.018 to 0.028 W/(m · K). Another material used as insulation is foamed polystyrene. Thermal conductivity factor of polyurethane foam is two times lower than that of polystyrene. The functional properties are better, too.

The problem of ozone depletion, which led to the establishment of the United Nations Environmental Program Protocol, also referred to as the Montreal Protocol, originally required a complete phase out of chlorofluorocarbon (CFC) and "soft" hydrochlorofluorocarbons (HCFC) as blowing agents before 2004. Neutral for the ozone layer are blowing agents based on hydrofluorocarbons (HFC), carbon dioxide or pentane isomers. Foams blown with derivatives of pentane, third generation blowing agents (HFC) and water are environ-

mentally friendly. They show ozone depletion potential (ODP) equal zero, low global warming potential, low or no toxicity, low thermal conductivity (*k*) and good physical properties of the resulting foams [1]. A great disadvantage of using pentane and its derivatives results from their high combustibility, which additionally increases the flammability of polyurethane foams [2, 3]. Introducing to polyurethane systems new reactive flame retardants based on halogen and phosphorus polyols [4–7] and chemical modification of polyurethane by introducing of isocyanurate rings (practical solutions used widely in USA), and also newly developed carbodiimides [8–10] will make polyurethane foams highly fireproof. Red phosphorus also had been known as a highly effective flame retardant in many polymeric applications for more than 20 years. Its flame retarding effect reduces the formation of toxic smokes and the heat release rate, preventing the outbreak of large fires even from small ignition sources. It has found its most important application in the flame retardancy of glass fibre reinforced polyamides (and also other polymers as polyethylene, polypropylene, high-impact polystyrene, polybenzothiazole etc.) where its high efficiency at low loading guaranteed the maintaining of excellent application properties while obtaining the highest flame proofing characteristics. However, the use of flame retarded rigid polyurethane foams (alone and with synergistic flame retardant systems) was not investigated and not reported in the literature. Authors show in this paper that red phosphorus together with isocyanurate rings in the structure of the foam create also very effective fire retarding system in the case of polyurethane foams. This

<sup>1)</sup> Central Institute for Labour Protection, ul. Czerniakowska 16, 00-701 Warsaw, Poland.

<sup>2)</sup> Centre for Materials Research & Innovation, Bolton Institute, Deane Road, b13 5ab Bolton, Greater Manchester, United Kingdom.

<sup>\*)</sup> Author to whom all correspondence should be addressed: tel.: +48 (22) 6234693, fax: +48 (22) 6214439, e-mail: wozat@ciop.pl

finding increases the possibility of many applications especially in building and mining sectors.

## EXPERIMENTAL

### Materials

The systems consist of components A and B. Component A is a group of substances containing polyols, catalyst, blowing agent, surfactant and flame retardant. Three kinds of polyols were used (all from Polish Chemical Company "Rokita"):

— Rokopol LM-2 is an aromatic amine sucrose based polyether polyol recommended for production of rigid polyurethane foams. Hydroxyl value was 478 mg KOH/g.

— Rokopol RF551 is a general purpose polyether polyol, on the base of modified sorbitol; recommended for production of CFC reduced rigid polyurethane foams. Hydroxyl value was 420 mg KOH/g.

— Rokopol PT44 — is an aliphatic polyoxypropylene polyol. Hydroxyl value was 425 mg KOH/g.

ols. Hydroxyl value was approximately 80 mg KOH/g and phosphorus content 43.0—48.0 %.

Component B is polymeric diphenylmethane — 4,4'-diisocyanate (PMDI) characterized by 31.47 % of NCO groups and functionality equal 2.55 (Alfa System in Brzeg Dolny, Poland).

### Preparation of rigid polyurethane (PUR) and polyurethane-polyisocyanurate (PUR-PIR) foams

The foams were obtained by one-stage method from the two-component (A-B) system with isocyanate index equal 1.1 in the case of PUR systems and for PUR-PIR systems this index was 3. The compositions of ten prepared foams are presented in Table 1. The component A was obtained by precise mixing (1800 rpm) of combination of polyols, catalyst, blowing agents, surfactant, and Exolit RP 652. In the component A the part of theoretically estimated quantity of red phosphorus was from 0 to 17 % in both PUR and PUR-PIR systems. The quantity of trimerization catalyst was calculated to be in excess of isocyanate. The surfactant quantity was two time

Table 1. The compositions of the reaction mixtures used to prepare PUR and PUR-PIR foams

Components	Number of sample									
	PUR foams					PUR-PIR foams				
	1	2	3	4	5	6	7	8	9	10
content, g										
PT44	35	31.12	27.23	23.35	19.46	35.00	32.31	29.62	26.93	24.23
LM 2	40	35.56	31.12	33.3	22.24	40.00	36.92	33.85	30.77	27.69
RF-551	25	22.23	19.45	16.67	13.90	25.00	23.01	21.16	19.23	17.31
RP 652	—	11.1	22.2	33.3	44.4	—	11	22.2	33.3	44.4
PC TD 34	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
PC STAB <sup>®</sup> SN 55	1.25	1.25	1.25	1.25	1.25	2.5	2.5	2.5	2.5	2.5
Water	1	1	1	1	1	1	1	1	1	1
Pentane	20	20	20	20	20	20	20	20	20	20
PMDI	131.77	119.71	107.65	95.58	83.52	329.40	299.30	269.11	238.96	208.80
PC Q1	—	—	—	—	—	9.43	8.22	7.01	5.81	4.61

As a catalyst PC TD *i. e.* 33 % solution of 1,4-diazabicyclo octane (Nitroil Europe) was used. As a trimerization catalyst for isocyanurate rings PC CAT<sup>®</sup> Q1 which was quaternary ammonium salt (Nitroil Europe) was applied.

*n*-Pentan (Fluka) as a blowing agent and PC STAB<sup>®</sup> SN 55 as silicon based surfactant (Nitroil Europe) were also applied.

As a flame retardant Exolit RP 652 (Clariant) characterized by hydroxyl value equal approximately 80 mg KOH/g, based on a specially treated red phosphorus (43-48 wt. %) was added. Exolit RP 652 has been developed as a flame retardant for polyurethanes used in electrical applications. Due to its high phosphorus content the product is a very effective flame retardant. The castor oil carrier is compatible with a wide range of poly-

higher in PUR-PIR formulations. The component B was PMDI. The two components was mixed and poured onto an open tray. Additionally PUR and PUR-PIR foams of reference without flame retardants (foams number 1 and 6 in Table 1) were prepared.

### Methods of testing

Temperature of reaction was measured by the thermocouple type K.

Technological times — start times, growth times and gelation times were measured by using stopwatch. Start time was characterized as time from mixing of the components to start of increase in volume. Growth time was measured for finish growth of volume for frothed foam.

When the foams had a hard surface than the gelation time was determined.

According to Polish and international standards the following properties were determined:

- apparent density — PN-92/C-89046 (ISO 845-1988)
- water absorption — PN-93/C-89084 (ISO 2896:1987)
- oxygen index — PN-76/C-89020 (ASTM D 2863-74).

## RESULTS AND DISCUSSION

The polymers obtained were characterized by change of utility properties in cause of use flame retardant in comparison with PUR and PUR-PIR foams. All properties are shown in Table 2.

The technological times are shorter in the case of PUR-PIR systems (samples 6–10) and in the cases of both kinds of foams for increase in the load of the red

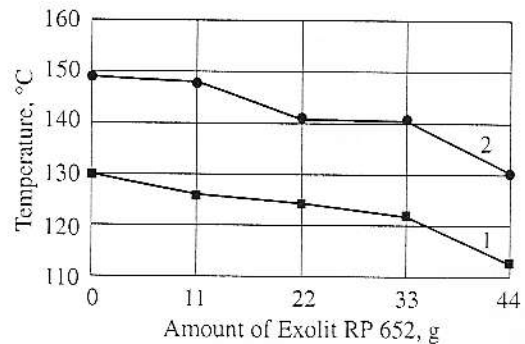


Fig. 2. Change of maximal temperatures of foaming process for PUR (1) and PUR-PIR (2) systems with increase in amount of Exolit RP 652.

of Exolit RP 652 in PUR foams does not cause deterioration in the functional properties *i.e.* water absorption and foam mass decrement.

With an increase in Exolit RP 652 content also oxygen index of synthesized foam increases what is shown in

Table 2. Basic functional properties of PUR and PUR-PIR foams obtained

Number of sample	Start time, s	Growth time, s	Gelation time, s	Maximum temperature of foaming process, °C	Apparent density, kg/m <sup>3</sup>	Water absorption, %	Foam mass decrement, %	Oxygen index, % O <sub>2</sub>
1	31.0	155.0	200.0	129.9	26.90	5.17	1.52	19.9
2	33.0	135.0	180.0	126.1	25.76	4.64	3.39	22.4
3	35.0	120.0	155.0	117.8	24.69	3.88	5.76	24.5
4	38.0	140.0	180.0	121.7	24.80	4.58	6.19	25.2
5	42.0	120.0	140.0	112.8	23.12	3.40	4.16	25.3
6	23.0	50.0	50.0	148.5	36.67	1.69	3.365	22.1
7	23.0	52.0	53.0	147.5	35.97	2.65	3.4	24.4
8	23.0	60.0	65.0	130.8	35.33	1.34	3.616	25.3
9	23.0	65.0	75.0	140.6	34.13	1.21	4.327	25.8
10	25.0	75.0	90.0	130.2	32.29	1.77	4.646	26.5

phosphorus. Low apparent density was obtained with the addition of 1 % of water as blowing agent supporting n-pentan. High amount of flame retardants and excess of isocyanate in PUR-PIR formulations caused increase in density to above 30 kg/m<sup>3</sup>. Application of high amount

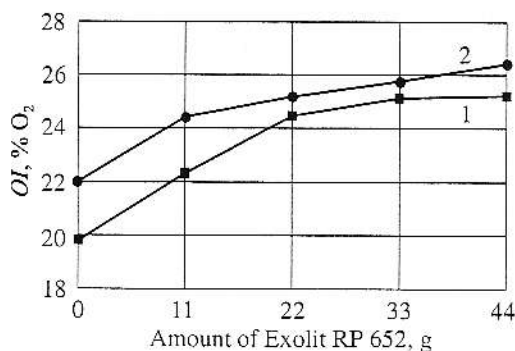


Fig. 1. Influence of amount of Exolit RP 652 on oxygen indexes (OI) of PUR (1) and PUR-PIR (2) systems.

Fig. 1. The PUR foams showed lower value of oxygen index (about 2 units) than PUR-PIR foams. Addition of Exolit RP 652 has an effect also on maximum temperature of foaming process what is illustrated in Fig. 2. This temperature decreases with increase in Exolit RP 652 amount. Apart from the amount of flame retardant influence, the maximum temperature of foaming is lower for PUR than for PUR-PIR foams.

## CONCLUSION

Foams combustion have been reduced by application of a bromine-free phosphorus system and isocyanurate rings in the structure of foams. PUR-PIR foams are less flammable than conventional PUR foams. The difference in value of oxygen index of foams is about 2 units in foams containing the isocyanurate rings favour.

— For comparison of PUR and PUR-PIR foams properties the tested mixtures contained the same quantities

of phosphorus flame retardant. Differences were in the quantities of PMDI used.

— PUR-PIR foams obtained with red phosphorus show better functional properties than classical PUR foams.

We can propose to use PUR-PIR foams obtained for: heat and cool insulations in heat distribution pipelines, refrigerators, freezers, pavilions, kiosks, spray insulating of buildings, automotive industry, aircrafts and ship industries, sport applications and plugging in mines.

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#### W kolejnym zeszycie ukażą się m.in. następujące artykuły:

- Teoretyczny model polimeryzacji hiperrozgałęzionej. Cz. II. Średni stopień polimeryzacji i wskaźnik polidispersyjności (*j. ang.*)
- Sieciowanie kauczuku butadienowo-akrylonitrylowego disulfidem tetraizobutylioturamu
- Możliwości wykorzystania gliceryny w doborze składu piankowych układów poliuretanowych
- Analiza wpływu składników wodnej dyspersji plastizoli PVC na jej stabilność
- Badanie zależności czasu relaksacji podłużnej w metodzie  $^1\text{H}$  NMR od struktury polidimetylosiloksanów i optymalizacja parametrów rejestracji widm
- Zmiany struktury włókien dibutyrylochitynowych w procesie regeneracji chityny (*j. ang.*)
- Efektywność procesu wytłaczania a charakterystyka dyszy stożkowo-walcowej głowicy wytłaczarskiej
- Badania procesu pulweryzacji metodą ścinania w stanie stałym w warunkach różnych przepływów ścinających