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Rigid polyurethane foams moulded with new generation blowing agents

RAPID COMMUNICATION

Summary — Rigid polyurethane foams were moulded with using cyclopentane, HCFC 141b and HFC 365/227 as physical blowing agents. Formulations with various amounts of blowing agents were elaborated and foams showing different density were prepared. The effects of the type and content of blowing agent on the physical, mechanical properties and thermal conductivity of the foams while ageing were investigated. The type of blowing agent affected the profiles of property changes of foams versus density. It has been found that the foams blown with cyclopentane or HFC 365/227 showed, in comparison with those blown with HCFC-141b used up to now, similar or even sometimes better properties.

Key words: polyurethane foams, blowing agents, properties, ageing.

The phase-out of HCFC-141b (containing Cl) as a blowing agent for rigid polyurethane foams is scheduled to begin in 2003. The modern refrigeration industry requires application of insulating materials with the possibly lowest thermal conductivity coefficient. Pentanes and hydrofluorocarbons have been identified as new generation blowing agents for polyurethanes to replace HCFC-141b [1—4].

Cyclopentane is a good candidate because of its low cost and gas thermal conductivity [5, 6]. However, major drawback of cyclopentane in comparison with the hydrofluorocarbons is its higher boiling point, which can result in the problem of foam dimensional stability at low temperature. Increase of the minimal applied density is necessary in order to obtain stable foams [6].

The aim of this work was to obtain the materials with suitable physical-mechanical properties for refrigeration applications.

EXPERIMENTAL

Materials

The materials used for foam preparation are listed below, specifying the characteristics of the various components:

— Alfapol TD-34 (Alfa Systems Sp. z o.o., Brzeg Dolny, Poland) — polyol based oxyalkylated *o*-tolylene diamine, hydroxyl number = 420 mg KOH/g;

— Alfapol G-1000 (Alfa Systems Sp. z o.o., Brzeg Dolny, Poland) — polyoxypropylene triol, hydroxyl number = 160 mg KOH/g;

— Alfapol RF-551 (Alfa Systems Sp. z o.o., Brzeg Dolny, Poland) — polyether polyol on the base of modified sorbitol, hydroxyl number = 420 mg KOH/g;

— Suprasec DNR (I.C.I. Ltd.) — oligomeric diisocyanatodiphenylmethane (polymeric MDI);

— SR-321 (Witco) — silicone surfactant;

— DMCHA (Texaco) — dimethylcyclohexylamine catalyst;

— Blowing agents:

— cyclopentane (Exxon) — CP,

— HCFC 141b (1,1-dichloro-1-fluoroethane) (Solvay Fluor GmbH),

— mixture of HFC 365/227 (93 wt. % of 1,1,1,3,3-pentafluorobutane and 7 wt. % of 1,1,1,2,2,3,3-heptafluoropropane) (Solvay Fluor GmbH).

Foams preparation and characteristic

The polyol component consists of the mixture of polyols (good miscibility with applied blowing agents), surfactant, water and catalyst. The blowing

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agent and isocyanate component (polymeric MDI) added to polyol component.

The mixtures of these components were stirred for 10 s with an overhead stirrer and then dropped into the mould (60×60×4 cm).

Three series of compositions differing in blowing agents contents were obtained for each blowing agent. Table 1 presents the compositions of reference series samples. Two other series samples contain, in comparison with reference ones, +25 wt. % or -25 wt. % of blowing agents.

Table 1. Formulations of reference samples

Components	Foam formulations, g		
	1	2	3
Polyol mixtures	100	100	100
Water	1.5	1.5	1.5
Surfactant	1.5	1.5	1.5
Catalyst	1.9	1.9	1.9
Blowing agent	12 (CP)	20 (HCFC-141b)	24 (HFC-365/227)
Polymeric MDI	124.8	124.8	124.8

The quantities of blowing agents were properly chosen in order to obtain polyurethane foams with comparable densities about 35—45 kg/m^3. The foams were conditioned at 20°C and 65% relative humidity for 24 hours, before being cut to test their physical-mechanical properties in accordance with Polish Standard (PN) tests (proper ISO Standard in brackets):

— Apparent density (kg/m^3) — PN-80/C-89035 (ISO 845).

— Compressive strength 10% (kPa) — PN-93/C--89071 (ISO 844); samples were compressed along the side 50 mm (horizontal direction).

— Closed cells (%) — PN-ISO 4590.

— Water absorption (%) — PN-69/C-89084 (ISO 2896).

— Dimensional stability (%) — PN-69/C-89083 (ISO 2796); investigations were realized in low temperature (samples were kept at temp. -25°C for 24 hours).

Thermal conductivity factors — λ [mW/(m · K)] were estimated using Laser Comp Heat Flow Instrument Fox 200 (temperature of cold plate 0°C and warm plate 20°C).

RESULTS AND DISCUSSION

As it was mentioned before, three series of foams with different contents of three used blowing agents were prepared in order to estimate the influence of cyclopentane and hydrofluorocarbons on the structure and properties of foams. The properties of the foams blown with cyclopentane and hydrofluorocarbons were compared with the properties of the products blown with HCFC-141b.

The decrease in blowing agent quantity made possible to obtain the products showing better mechanical properties, but higher density, which is not favourable from economical point of view. However, the increase in blowing agent quantity caused important decreasing of compressive strength of the foams prepared. For better comparison of mechanical properties of foamed products the factor *CS/D* — the ratio of compressive strength and density — was calculated. The values of calculated *CS/D* factor for prepared polyurethane foams are presented in Fig. 1. As it is shown in this figure, the differences between particular samples are rather small (the biggest in case of reference samples).

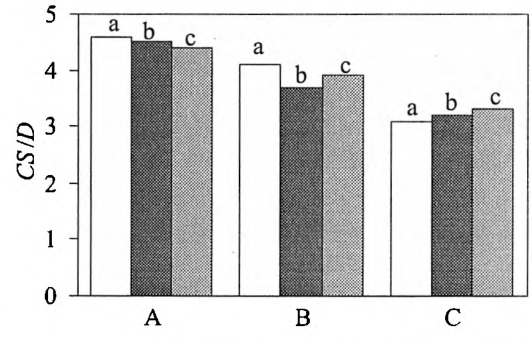

Fig. 1. CS/D ratio versus blowing agent content, 1 — respectively blowing agent numbers

In the case of reference materials (B) and compositions containing 25 wt. % less of blowing agent (A) the highest values of *CS/D* were observed for foams with cyclopentane. The decrease in foam density by applying of larger amount of blowing agent (C) caused the decrease in *CS/D* factor of foams. Generally, the profiles of *CS/D* changes versus foam density are similar for products with all blowing agents used. The increase in various blowing agents amounts by 25 wt. % has caused significant worsening of *CS/D* factor.

Table 2. Physical properties of reference materials

Property	Foam No (according Table 1)		
	1	2	3
Apparent density, kg/m^3	39.7	37.3	37.8
Closed cells, %	95—98	96—97	95—98
Water absorption, wt. %	2—2.2	2—2.2	2—2.2
Dimensional stability, %	-0.6	-1.1	-1.1
λ-value after 24 h, mW/(m · K)	22.8	21.3	22.9

The physical properties of reference foams are presented in Table 2. Density of the polyurethane blown with cyclopentane is the highest and the dimensional stability of this foam is the most favourable. The kind of blowing agent does not influence the water absorption and percentage of closed cells. The thermal conductivity factor measured after 24 hours was the lowest for the polyurethane blown with HCFC-141b (2).

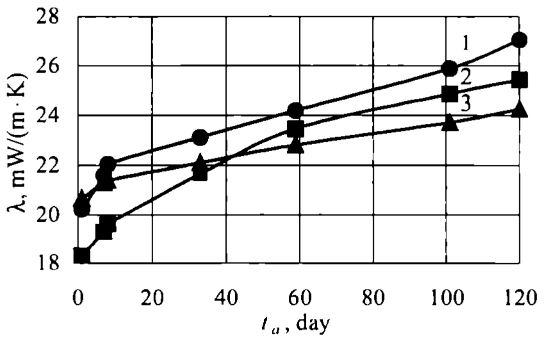

Fig. 2. Changes of thermal conductivity (λ) of polyurethanes blown with different agents while ageing (t_a): 1 — cyclopentane, 2 — HCFC-141b, 3 — HFC 365/227

The values of thermal conductivity of foams were changing gradually during long ageing (Fig. 2). Increasing of λ is strongly influenced by blowing agent diffusion from the foam. The lowest diffusion rate of blowing agent was observed in the case of HCF 365/227 (curve 3). Therefore, after 120 days period the materials foamed with this agent show more favourable thermoinsulating properties. It can results from the agent molecular size and chemical constitution.

CONCLUSIONS

Rigid polyurethane foams blown with cyclopentane and mixture of hydrofluorocarbons show very good mechanical properties and dimensional stability. With regard to this, the foams are equal and sometimes better than those blown with HCFC-141b.

From economical point of view it is more beneficial to use cyclopentane in refrigeration application, in which the special properties concerning flammability are not required.

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