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Studies on utilization of wheat slops for production of rigid polyurethane-polyisocyanurate foam

RAPID COMMUNICATION

Summary — Solid parts of the wheat slops were applied as a filler (5—30 wt. % in relation to the sum of polyisocyanate and polyether polyol masses) in polyurethane-polyisocyjanurate (PUR-PIR) composition. Six foams containing different amounts of slops were prepared and then, their physical and mechanical properties *i.e.* apparent density, compressive strength, brittleness, combustion residue, stability of linear dimensions, change of volume, weight loss (48 h, temp. 120 ^{o}C), softening point, content of the closed cells and absorbability of water were determined. Moreover, the foams were subjected to thermogravimetric and infrared (IR) analyses. The results proved that waste wheat slops can be useful as a filler for preparation of rigid PUR-PIR foams.
Key words: rigid polyurethane-polyisocyanurate foams, wheat slops, filler, physical properties, mechanical properties, thermal properties.

BADANIA NAD WYKORZYSTANIEM WYWARU PSZENNEGO DO PRODUKCJI SZTYWNEJ PIANKI POLIURETANOWO-POLIIZOCYJANUROWEJ

Streszczenie — Części stałe wywaru pszennego stosowano jako napełniacz (5—30 % mas. w stosunku do sumy mas poliizocyjanianu i poliolu polieterowego) w kompozycji poliuretanowo-poliizocyjanurowej (PUR-PIR). Otrzymano w ten sposób sześć pianek różniących się zawartością wywaru (tabela 1), które poddano badaniom właściwości fizycznych i mechanicznych. Zmierzono ich gęstość pozorną, wytrzymałość na ściskanie, kruchość, pozostałość po spaleniu, stabilność wymiarów liniowych, zmianę objętości, ubytek masy (48 h, temp. 120 ^{o}C), temperaturę mięknienia, zawartość komórek zamkniętych, chłonność wody oraz wykonano analizę termograwimetryczną i w podczerwieni (IR) (tabela 2). Wyniki badań dowodzą, że odpady wywaru pszennego mogą być użyte jako napełniacz do produkcji sztywnych pianek PUR-PIR.
Słowa kluczowe: sztywne pianki poliuretanowo-poliizocyjanurowe, wywar pszenny, napełniacz, właściwości fizyczne, właściwości mechaniczne, właściwości termiczne.

The history of polyurethanes is relatively short but during about 70 years they became one of the most dynamically developed groups of polymers. They are applied practically in all branches of polymer industry such as: foams, elastomers, thermoplastics, hardening plastics, adhesives, coatings, leak stoppers, fibres and so on [1, 2].

Polyurethanes are used almost in each branch of industry and they contribute to the change of human life quality. Furniture, mattresses, car seats, shoe soles, thermal insulation for refrigerators and buildings, imitation of wood, packing or coatings are only some examples of polyurethane applications in everyday life. The substantial part of them is manufactured in a form of rigid polyurethane foams.

In order to reduce the costs of production of the rigid polyurethane foams and simultaneously to improve some of their physical and mechanical properties, the different fillers are applied for their preparation [7—12].

The distillery slops are by-product obtained in agricultural distilleries and the management of its total amount cause difficulties. That is why the utilization of the mentioned by-product aroused scientists' interest for a long time [12, 13].

The aim of this paper is study on utilization of the solid fraction of the wheat slops for preparation of rigid polyurethane-polyisocyanurate (PUR-PIR) foams. The wheat slops are applied as a filler in order to reduce the costs of foam production and simultaneously to improve some physical and mechanical properties of the foams.

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EXPERIMENTAL

Materials

The following components were used for preparation of rigid PUR-PIR foams:

— Rokopol RF55, which is polyether polyol obtained as a product of oxypropylation of sorbitol with acidity number L_{OH} = 495 mg KOH/g (Alfasystems, Brzeg Dolny, Poland).

— Silicon L6900 is polysiloxypolyalkyleneoxydimethylene copolymer used as surfactant (Witco, Sweden).

— Catalyst 12 is 33 wt. % solution of potassium acetate in diethylene glycol applied to foams (KChiTP, UKW, Bydgoszcz, Poland).

— DABCO 33LV is 33 wt. % solution of triethylenediamine [1,4-diazobicyclo(2,2,2)octane] in dipropylene glycol, applied to foams as a cocatalyst (Germany).

— Antiblaze TMCP is tri(2-chloro-1-methylene-ethylene)phosphate (Albright and Wilson, Great Britain) used as a flame retardant.

— Ongromat 20-30 is polyisocyanate with NCO groups content equal 31 %.

— Solid fraction of wheat slops (Cargil, Bielany Wrocławskie, Poland).

Solid fraction of wheat slops applied in our studies was obtained by fermentation of the wheat starch milk (17.1 wt. % of starch, 16.2 wt. % of dry mass). The slops dry mass consisted of raw fat (9.87 wt. %, PN-ISO 6492:2005), raw fibre [4.07 wt. %, PN-EN ISO 6865:2002 (U)], proteins (24.99 wt. %, PN-92/R-64811) and mineral compounds (3.92 wt. %). Chemical composition of mineral compounds in wheat slops was as follows: phosphorus (0.84 wt. %, PN-ISO 6491:2000), sodium (1.04 wt. %, PN-R-64782:1994) and chlorine (0.63 wt. %, PN-93/R-64750). Solid fraction was separated from water in Büchner funnel, dried in blast drier at temperature of 100 °C and then, it was ground in a ball mill. The obtained solid contained 6.7 wt. % of humidity (balance-drier, PN-76/R-64752) and its color was brown. In order to obtain rigid PUR-PIR foams, the solid fraction with grain dimensions of 1mm was used (sieve analysis, PN-71/C-04501).

Preparation of rigid PUR-PIR foams

The rigid PUR-PIR foams were obtained in a laboratory scale by one-stage method from the two-component (A + B) system at the equivalent proportion of NCO and OH groups equal from 3:1 to 3:2.2. The component A was composed from 60.0 g of Rokopol RF55, 5.2 g of Silicon L6900, 3.1 g of DABCO 33LV, 7.2 g of Catalyst 12, 51.6 g of Antiblaze TMCP, 3.8 g of distilled water and solid fraction of wheat slops was added in amount ranging from 5 to 30 wt % (in relation to the sum of polyisocyjanurate and polyether polyol masses). The component B was polyisocyanate Ongromat 20-30 in amount of 284.0 g. The components were mixed (1800 rpm) at respective weight ratios and poured onto an open rectangular tray. After foaming, the foams were thermostated for 4 h at the temperature of 120 °C; then the foams were seasoned for 48 h at the temperature of 20 ± 4 °C. In that manner, one standard foam without a filler and six foams containing different amounts of solid fraction of wheat slops as a filler (see Table 1) were prepared.

T a b l e 1. Contents of solid fraction of wheat slops in different samples of the rigid PUR-PIR foams

Symbol of foam sample	Amount of solid fraction of wheat slops	
	g	wt. %[a)]
0	0	0
1	17.2	5.0
2	34.4	10.0
3	51.6	15.0
4	68.8	20.0
5	86.0	25.0
6	103.2	30.0

[a)] Concentration is expressed in relation to the sum of polyisocyanate and polyether polyol masses.

Methods of testing

After seasoning, the foams were cut and their fundamental properties were determined according to the obligatory standards. Each type of the system prepared was subjected to four times control foaming.

The PUR-PIR foams were analyzed by IR spectroscopy (KBr technique, a Vector spectrometer, Brucker, range from 400 cm^{-1} to 4000 cm^{-1}).

The thermogravimetric analysis was done in air atmosphere at the heating rate of 5 deg/min at temperature ranging from 20 °C to 800 °C. Tests were carried out using derivatograph produced by MOM Budapest (Paulik-Paulik-Erdey).

RESULTS AND DISCUSSION

Rigid foams prepared with addition of solid fraction of wheat slops were characterized by the longer times of processing. Start time was ranging from 16 s for standard foam to 38 s for the foam containing 30 wt. % of a filler, time of expansion was from 18 s for standard foam to 49 s for foam containing 30 wt. % of a filler and times of gelation did not exceed 75 s for all foams.

Increase in amount of solid fraction of wheat slops in foam composition from 5 to 30 wt. % in relation to the sum of polyether polyol and polyisocyanate masses resulted in a distinct decrease in the foam apparent density from 36.96 kg/m^3 for standard foam to 25.6 kg/m^3 for the foam containing the highest amount of slops. As

T a b l e 2. Fundamental functional properties of the rigid PUR-PIR foams

Characteristics	Number of foam						
	0	1	2	3	4	5	6
Density (ISO 845-1988), kg/m^3	36.96	35.2	33.9	30.6	28.6	26.1	25.6
Compressive strength in direction of foam expansion (ISO 844:1993), kPa	221.7	192.3	160.5	144.3	106.1	92.6	79.0
Brittleness (ASTM C-421-61), %	41.9	40.5	29.8	27.4	24.6	20.4	16.9
Retention (ASTM D3014-73)	76.6	69.7	61.2	52.6	44.7	39.2	31.9
Softening point (DIN 53 424), ^{o}C	230	230	227	225	221	223	221
Content of closed cells (PN-ISO 4590:1994)	83.4	88.9	85.3	81.7	76.5	69.3	64.7
Weight loss after 48 h at 120 ^{o}C, %	1.1	1.1	1.2	1.2	1.2	1.3	1.3
Change in linear dimensions after 48 h at 120 ^{o}C, %	-0.1	-0.6	-0.6	-0.8	-0.8	-0.8	-0.8
Change in volume after 48 h at 20 ^{o}C, %	-0.5	-1.0	-1.0	-1,2	-1.2	-1.2	-1.2
Absorbability of water (DIN 53 433)	1.8	2.03	2.1	2.5	2.9	3.3	3.5

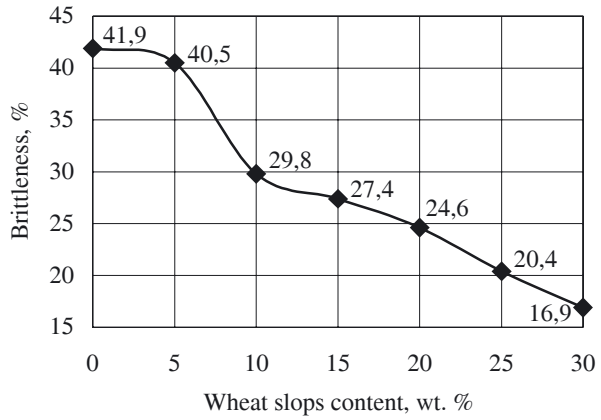

Fig. 1. The effect of content of solid fraction of wheat slops on brittleness of rigid PUR-PIR foam

the content of slops in the foam increased the compressive strength determined in direction of foam expansion was reduced from 221.7 kPa (standard foam) to 79.0 kPa (sample 6).

As it was shown in Figure 1 the distinct reduction in foam brittleness from 41.9 % (standard foam) to 16.9 % was observed when the content of wheat slops was increased in foam composition. However, softening point only slightly decreased from 230 ^{o}C (standard foam) to 221 ^{o}C (sample 6). The content of a filler influenced also the combustion residue (retention) significantly decreasing this value from 76.6 % for standard foam to 31.9 % for sample 6.

Change in linear dimensions, volume and weight loss of the foam after 48 hours at temperature of 120 ^{o}C were practically independent on the content of solid fraction of wheat slops in PUR-PIR foams. Change of linear dimensions was determined only in direction in the foam expansion.

As a result of thermogravimetric analysis, it was found that extrapolated temperature of beginning of the main weight loss of the foams containing slops in relation to the standard foam was unchanged (about 220 ^{o}C). However, maximum rate of the foam weight loss was within the range of temperatures from 290 ^{o}C (sample 0) to 305 ^{o}C (sample 6). IR analysis confirmed the presence of bands characteristic for isocyanurate (1710 cm^{-1}—1690 cm^{-1}) and urethane (1740 cm^{-1}—1700 cm^{-1}) bonds.

CONCLUSIONS

The results of our studies proved that the waste distillery slops could be successfully used as the fillers for rigid polyurethane-polyisocyanurate foams.

On account of the industrial application of rigid polyurethane foams, their brittleness is a very important property. The obtained foams were characterized by the considerably reduced brittleness (16.9 % for foam with 30 wt. % of filler) in comparison to standard foam without a filler (41.9 %) and it was achieved by increasing the content of solid fraction of wheat slops. Other properties of the foams after introducing the filler into the composition were only slightly deteriorated in comparison to the standard foam.

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Received 24 I 2007.

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

— Zdolność do polimeryzacji cyklicznych estrów alifatycznych
— Modyfikacje polimerów siloksanowych
— *N*-winyloformamid — nowy ekologiczny monomer wodorozpuszczalny
— Reakcje interelastomerowe w niekonwencjonalnych mieszaninach elastomerów
— Kompozyty polimerowe podatne na (bio)degradację
— Zastosowanie żywic epoksydowych w elektronice i optoelektronice. Cz. III. Żywice epoksydowe o nieliniowych właściwościach optycznych
— Dyspersja napełniacza w mieszance gumowej. Cz. I. Opis procesu dyspergowania
— Barwniki styrylochinoliniowe jako sondy spektroskopowe w procesie polimeryzacji rodnikowej
— Azowe inicjatory funkcyjne — rozpad termiczny w mieszaninach akrylonitryl/*N,N*-dimetyloformamid
— Wpływ promieniowania laserowego na cienkie błony kolagenowe. Cz. II. Badania spektroskopowe struktury „mikropianki" kolagenowej
— Glikoliza odpadów poliuretanowych. Cz. I. Środki glikolizujące i katalizatory
— Ocena poprawek w pomiarach reologicznych polimerów termoplastycznych. Cz. I. Poślizg przy ściance kanału