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Studies on utilization of potato slops in the production of rigid polyurethane—polyisocyanurate foams

RAPID COMMUNICATION

Summary — A potato slop (PS), 94% H_2O and 6% dry mass, a by-product in the process of making high wines, was used 5—30% by weight (based on total weight of polyisocyanurate and oligodiol) to modify rigid PUR-PIR foams (Table 1). Density, compressive strength, brittleness, oxygen index (OI), softening point, combustion residue, TGA thermograms (20—800°C), mass decrement, linear dimension stability, and 48-hour change in volume (at 120°C) were determined for the six foams prepared (Table 2). At 5—20% PS, foam's compressive strength, softening point, and combustion residue were unaffected but, at 25—30% PS, they decreased. Linear dimension, volume and mass decrements, and OI were unaffected, but brittleness decreased (Fig. 1). IR spectra showed the bands characteristic for isocynaurate and urethane. With 20% by wt. PS added, the PUR-PIR foam was the best, exhibiting reduced brittleness while other property data were like those for a standard foam (no PS added).

Key words: rigid polyurethane-polyisocyanurate foams, potato slop as filler, modification of rigid polyurethene-polyisocyanurate foams.

Potato slop is a by-product obtained in agricultural distilleries [1—3]. In Poland, the agricultural distilleries are not able to manage the total available quantity of the slops. A considerable portion of potato slops is poured out onto cultivable fields and this is a nuisance to natural environment. Total utilization of potato slops has been a problem for a long time [4].

This paper continues our studies on the modification of rigid polyurethane-polyisocyanurate (PUR-PIR) foams [5—9]. Potato slops were utilized to prepare rigid PUR-PIR foams. The potato slop was applied as a filler to reduce the production cost and to improve some properties of the foams [10—12].

EXPERIMENTAL

Potato slops applied for preparation of rigid PUR-PIR foams

The potato slop (94% of H_2O + 6% of dry mass) used in this study was a by-product obtained in the production of high wines from potato (Agricultural Distillery, Samoklęski n/Bydgoszcz, PL).

The dry mass contained: non-fermenting sugars, 3.1% (PN-R-64784:1999); fat, 0.05% (PN-76/R-64753); fibers, 0.7% (PN-87/R-64814); proteins, 1.45% (PN-92/R-64811); and mineral compounds, 0.7%. The chemical composition of the slops was: calcium, 3.0 g/kg (PN-93/R64750); phosphorus, 8.0 g/kg (PN-76/R-64781); iron, 1300 mg/kg (PN-59/A-04015); copper, 340 mg/kg (PN-80/A-04012); sodium, 1.1 g/kg (PN-R-64782:1994). Water was separated from solids on a Büchner funnel. The solids were dried in a blast drier at a temperature of 120°C and then ground in a ball mill. The water content of the resulting solid was equal to 5.5% (balance drier, PN-76/R-64752) and its color was brown. The slop, particle size 1 mm (sieve analysis, PN-71/C-04501), was applied to the preparation of rigid PUR-PIR foams.

Preparation and evaluation of rigid polyurethane-polyisocyanurate foams

The foams were obtained on a laboratory scale by a one-stage method from a two component (A-B) system at the equilibrium ratio of NCO to OH groups equal to 3:1. Component A was obtained by precisely mixing (1800 rpm) appropriate amounts of Rokopol RF-55, the

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

Materials	Characteristics (producer)	Unit	Foam No.						
			0	1	2	3	4	5	6
1. Rokopol RF-55	product of oxypropylation of sorbitol L_{OH} = 495 mg KOH/g (NZPO Rokita, Brzeg Dolny, Poland)	g	60.0	60.0	60.0	60.0	60.0	60.0	60.0
2. Silicone L6900	polysiloxypolyalkyleneoxydimethylene copolymer (Witco, Sweden)	g	5.2	5.2	5.2	5.2	5.2	5.2	5.2
3. DABCO 33LV	33% solution of triethylenediamine [1,4-diazobicyclo(2,2,2)octane] in dipropylene glycol, applied to foams (Germany)	g	3.1	3.1	3.1	3.1	3.1	3.1	3.1
4. Catalyst-12	33% potassium acetate in diethylene glycol applied to foams (ZTO ATR Bydgoszcz, Poland)	g	7.2	7.2	7.2	7.2	7.2	7.2	7.2
5. Antiblaze TMCP	fire retandant, tri(2-chloro-1-methylene-ethylene) phosphate (Albright and Wilson, Great Britain)	g	51.6	51.6	51.6	51.6	51.6	51.6	51.6
6. Potato slops		g	0	17.2	34.4	51.6	68.8	86.0	103.2
		%	0	5.0	10.0	15.0	20.0	25.0	30.0
7. Distilled water		g	3.8	3.8	3.8	3.8	3.8	3.8	3.8
8. Cosmonate 200 PDMI	polyisocyanate NICO groups, 31% (Japan)	g	284.0	284.0	284.0	284.0	284.0	284.0	284.0

Table 2. Basic functional properties of rigid PUR-PIR foams

Characteristics	Foam No.						
	0	1	2	3	4	5	6
Apparent density (PN-93/C-89046), kg/m^3	36.0	36.0	36.0	36.1	36.2	36.2	36.3
Compressive strength in the direction of foam expansion (PN-93/C-89071), kPa	196.1	196.0	195.3	195.9	195.1	180.6	180.2
Brittleness (ASTM 421-61), %	42.4	20.1	20.0	19.0	19.0	19.0	19.0
Oxygen index (PN-76/C-89020), %	24.7	24.9	24.9	24.9	24.9	24.7	24.7
Residue after combustion, %	91.8	91.5	91.4	90.4	90.5	79.3	78.2
Softening temperature (DIN-53424), °C	221.5	221.5	221.3	220.4	220.3	203.0	200.4
Foam mass decrement in 48 h at 120°C, %	1.1	1.1	1.1	1.2	1.2	1.2	1.2
Change of linear dimensions in direction of foam expansion in 48 h at 120°C, %	-0.3	-0.3	-0.3	-0.3	-0.3	-0.3	-0.3
Change of foam volume in 48 h at 120°C, %	-0.7	-0.7	-0.7	-0.8	-0.8	-0.8	-0.8

potato slop, catalysts, fire retardant, and a surface active agent. Component B was Cosmonate PMDI (Table 1). The two components, A and B, were mixed and poured onto an open rectangular tray. The resulting foams were thermostated for 4 h at a temperature of 120°C in a blast drier and then seasoned for 48 h at room temperature. The basic functional properties of the foams were determined according to Polish Standards (Table 2). Each type of foam was subjected to a double control of foaming. The PUR-PIR foams were analyzed by IR spectroscopy (KBr technique) by using a Vector instrument (Brucker). A thermogravimetric analysis was carried out by using a derivatograph (MOM Budapest, Hungary) operated in the Paulik-Paulik—Erday system in air at a heating rate of 5°C/min within the temperature range of 20°C to 800°C.

DISCUSSION

The compositions and the property data of the rigid PIR-PUR foams are presented in Tables 1 and 2, respectively.

The starting times of the foams obtained by using potato slops (PS) were within the range of 13 s to 17 s, whereas the foaming and gel times where shorter than 90 s.

As the amount of potato slops in these foams was increased from 5% to 30% by weight in relation to the total amount of polyisocyanurate and oligodiol, the apparent density of the foams did not change and was equal to 36.2±0.1 kg/m^3.

An increase in the potato slops content from 5% to 20% by weight in the foam (foams Nos. 1 to 4) had no effect on foam's compressive strength, softening temperature and combustion residue in relation to the standard foam (foam No. 0, no PS added) and the values were equal to 195.6±0.5 kPa, 220.9±0.6°C and 91.6±0.2%, respectively. As the amount of PS was increased from 25% to 30% by weight, the compressive strength of the foam decreased from 196.1 kPa (standard foam No. 0) to 180.6 kPa and 180.2 kPa (foams No. 5 and 6), the softening point decreased from 221.5°C (foam No. 0) to 203.0°C and 200.4°C (foams No. 5 and 6) and combustion residue dropped from 91.8% (foam No. 0) to 79.3% and 78.2% (foams No. 5 and 6).

The oxygen index remained practically unaffected by the PS content in the foams in relation to the standard foam and was equal to 24.8±0.1%. However, brittleness decreased from 42.4% (foam No. 0) to 19.0 (foams No. 3—6, Fig. 1).

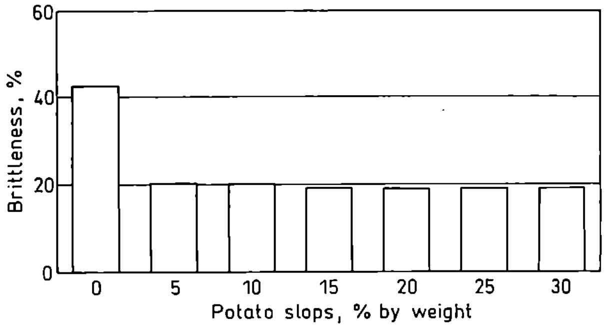

Fig. 1. Brittleness of the rigid PUR-PIR foams in relation to the amount of potato slops added

Changes in linear dimensions, volume and mass decrements after 48 h of thermostating at 120°C as well as thermal resistance remained practically unaffected by the PS content in the PUR-PIR foams. The extrapolated begin of the main mass decrement after addition of PS to the foam was unchanged in relation to the standard foam and its value was about 225°C (foams Nos. 0, 1—6). However, the highest rate of the foam mass decrement was within the range of temperatures from 300°C (for standard foam No. 0) to 310°C (for foam with 30% by weight of PS added).

IR spectroscopy of the PUR-PIR foams confirmed the presence of the bands characteristic for isocyanurate (1710 cm^{-1}—1690 cm^{-1} and 1410 cm^{-1}) and urethane (1740 cm^{-1}—1700 cm^{-1}) bonds.

Our studies have shown that waste potato slops can be useful as a filler for PUR-PIR foams. Foams characterized by reduced brittleness and other properties similar to those of the standard foam (with no PS added) were obtained when slops were added in amounts lower than 20% by weight.

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