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Material recycling of RIM flexible polyurethane foams wastes

Summary — A recycling method of RIM PUR foam wastes by controlled degradation during twin-screw extrusion has been developed. The process involves breakage of only cross-linking bonds (allophanate and/or biuret bonds) in the polymer. The essential factor that has to be controlled is *int. al.*, decreasing temperature profile along extruder cylinder (from fed hopper to die). The method provides thermoplastic elastomer of strength comparable to that of the original material. It can be injection molded or extruded into various products. Reactive co-extrusion of polyesterdiol based PUR wastes with PVC-U (5—10 wt. %) that yields homogeneous polymer blends of improved hardness has also been studied.

Key words: material recycling, PUR foams wastes, reaction injection molding, structure changes, PUR/PVC blends, mechanical properties.

The subject of this paper is a method of material recycling of cast microporous polyurethane (PUR) elastomers and their reshaping into pellet form. By standard methods the resulting granules can be processed again into thermoplastic polyurethane elastomer. Soft polyurethane microporous foams are produced mostly by reaction injection molding (RIM), where streams of polyesterdiol or polyetherdiol (depending on system used) are mixed within the head of processing machine with diisocyanate components (Fig. 1).

Fast reactions lead to foaming and solidification of the polymer directly within the mold. The reactions produce covalent bonds that result in both the growth of main chains and formation of cross-links (via allophanate and/or biuret groups) (Scheme A).

Reprocessing of RIM PUR wastes is quite difficult because they are not thermoplastic materials. Combustion of the wastes is hazardous to the environment due to toxic gases that are usually formed. Hence, the following methods have been proposed [1—12], for the cast PUR waste materials utilization:

— alcoholysis (or, more often, glycolysis) of polyurethane leading to oligomeric diols, that can then be reused in manufacturing of foams again by the RIM process [1—4];

— milling, usually at substantially reduced temperature, to micron-size particles that are added to the polyol stream of the RIM machine [1, 5—8];

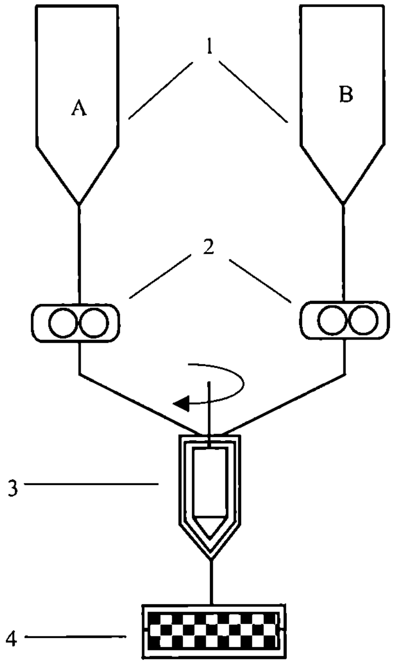

Fig. 1. The reaction injection molding process of PUR: 1 — component A (polyetherdiol or polyesterdiol + diol + additives) and component B (diisocyanate or oligomer with isocyanate end-groups), 2 — high pressure pump, 3 — mixing head, 4 — mold with reacting PUR mixture

— grinding (to particle sizes ~5—8 mm) and reactive sintering (or molding), often with extra addition of isocyanate prepolymers, to produce sound absorbing or insulating sheets [1, 9—11].

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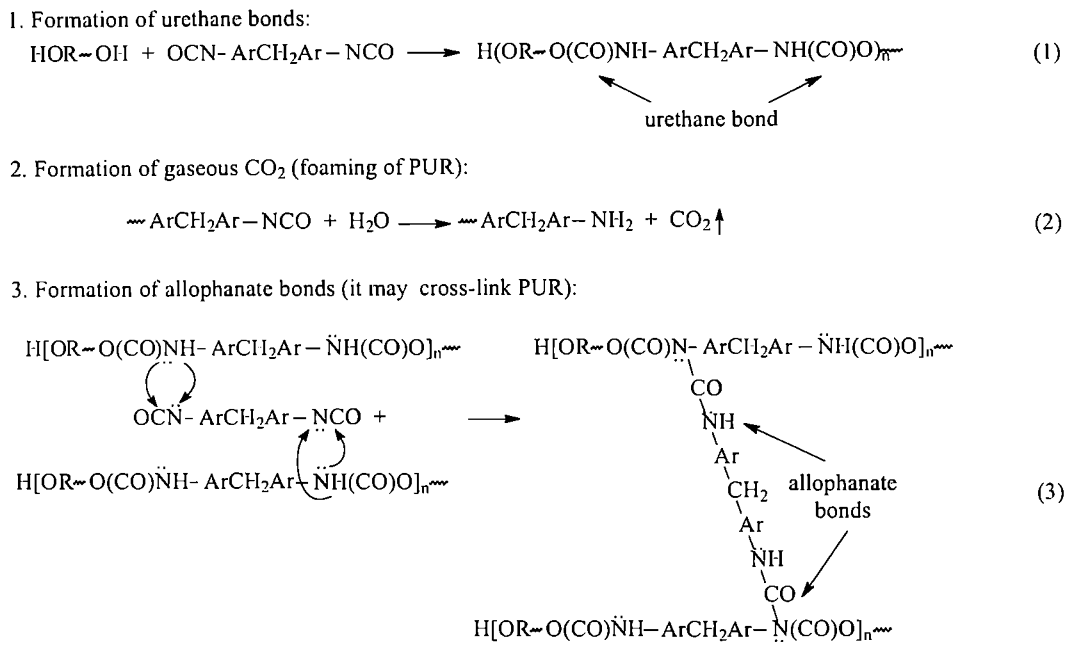

$$HOR\sim OH + OCN\text{-}ArCH_2Ar\text{-}NCO \longrightarrow H(OR\sim O(CO)NH\text{-}ArCH_2Ar\text{-}NH(CO)O)_n\sim \qquad (1)$$

$$\sim ArCH_2Ar\text{-}NCO + H_2O \longrightarrow \sim ArCH_2Ar\text{-}NH_2 + CO_2\uparrow \qquad (2)$$

Scheme A

Detailed study has shown [12] that PUR foams comprise only slightly cross-linked polymer, mostly with allophanate and biuret bonds. The stability of these groups at elevated temperature is considerably lower than that of urethane or ester/ether bonds. Allophanate and biuret bonds start to decompose already at temperature 120—130°C [13]. This property was used long ago to break cross-links during controlled degradation of PUR waste foams by processing them in screw extruders into thermoplastic products [12]. However, as we have found in preliminary tests, the thermoplastic material obtained this way had poor thermal stability and its mechanical properties varied considerably from batch to batch, despite of using the same extrusion parameters.

We have developed a laboratory-scale procedure of manufacturing well processed thermoplastic PUR elastomer of good mechanical strength [14]. We have used PUR wastes from shoe sole cast process with use of polyesterdiol based system Elastopan 7209 (Elastogran-BASF, Germany). A twin-screw extruder TSK 20 (Theysohn, Germany) with screws of diameter 20 mm was used. The extruder is shown schematically in Fig. 2. The crucial factors that had to be controlled in the method were following:

— suitable moisture of the recyclate,

— decreasing temperature profile along extruder cylinder (from feed hopper to die),

— suitable lubricant and thermal stabilizer applied to the extruder cylinder at some distance from the feed hopper, preferably in the place where the recyclate is already melted.

The delayed dosage of the additives aimed at increasing friction of particles of the degrading waste material in the initial part of extruder barrel, and then to prevent further undesired degradation in the part of machine, where polymer had already melted. The typical extrusion parameters were as follows:

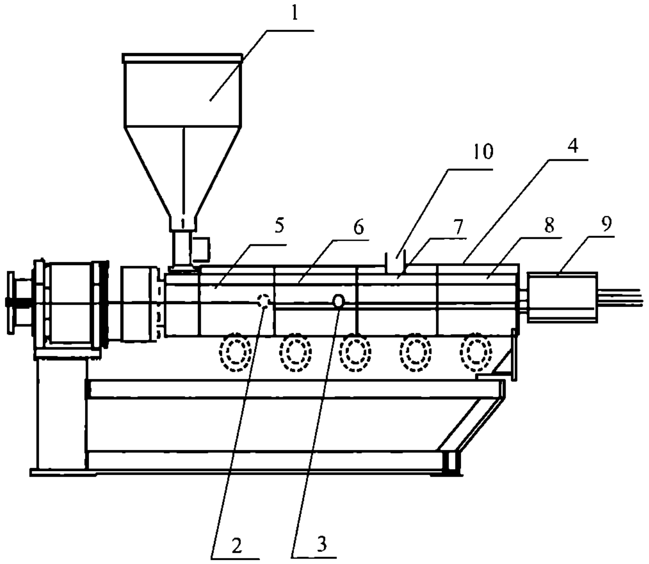

Fig. 2. Twin-screw extruder used for PUR recycling studies: 1 — hopper; 2, 3 — additional feed hole; 4 — extruder barrel; 5, 6, 7, 8 — segmented barrel sections; 9 — pelletizing die; 10 — degassing hole

— barrel temperature: 180 —155°C,

— die temperature: 155 °C,

— back pressure: 5—6 MPa,

— screw speed: 200—260 min^{-1},

— output: 5—6 kg/h.

DSC thermograms of PUR wastes (Figs. 3 and 4) show the presence of a small and broad endothermic

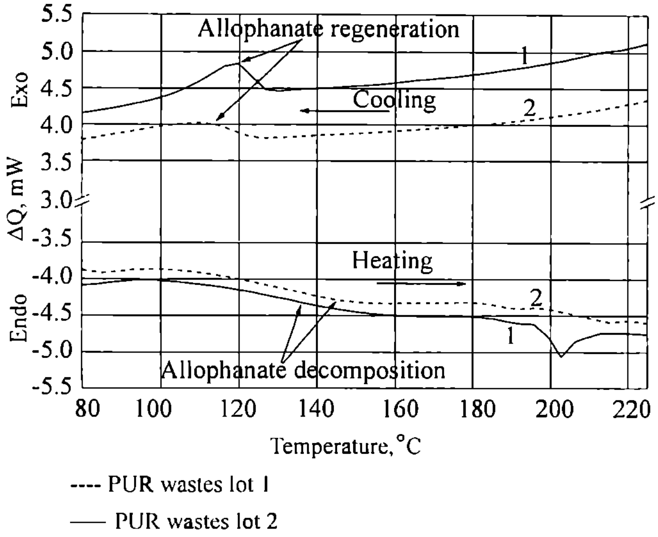

Fig. 3. DSC of PUR foams wastes: 1 — sample first, 2 — sample second; heating and cooling rate — 10 deg/min

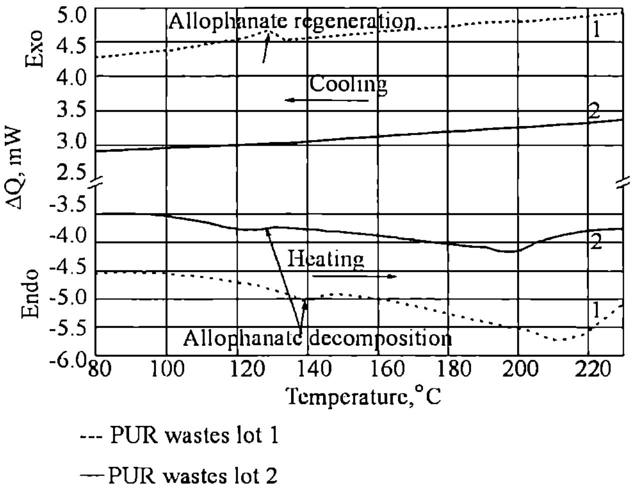

Fig. 4. DSC of PUR foams wastes after reactive extrusion: 1 — PUR foams wastes extruded, 2 — PUR foams wastes coextruded with 10 wt. % of unplasticized PVC (PVC-U); heating and cooling rate — 10 deg/min

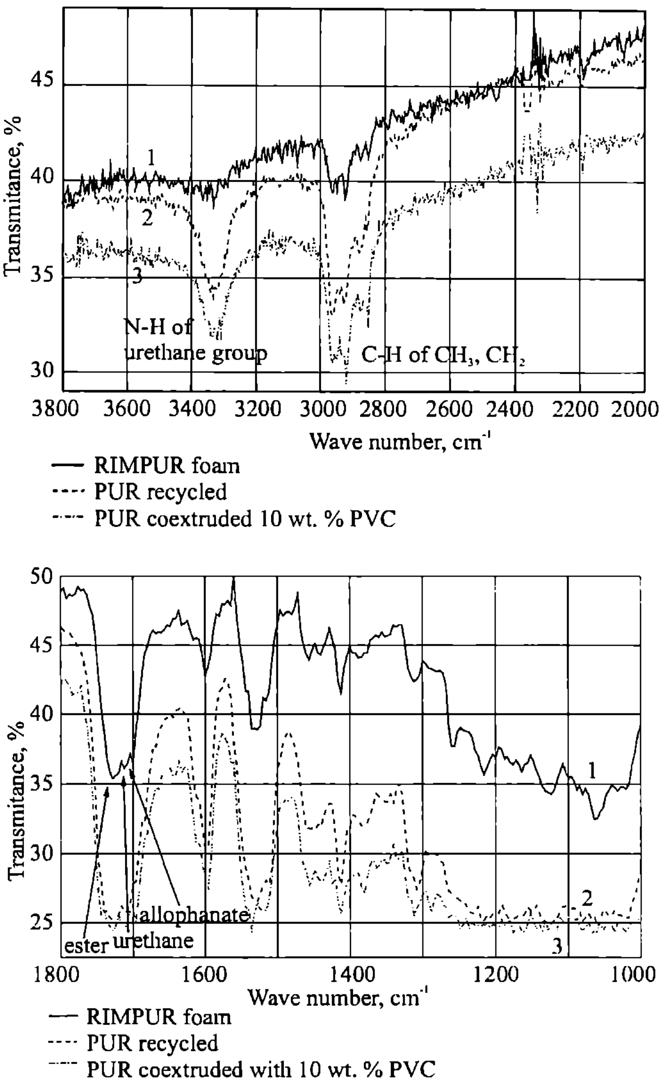

Fig. 5. IR spectra of original PUR foam wastes (1), its recycled blend (2) and recycled blend coextruded with 10 wt. % of PVC-U (3)

peak between 120 and 180°C that appears in the heating mode. It can probably be accounted for breaking of allophanate bonds. In the cooling mode curve, an exothermic peak appears between 130 and 100°C. We believe this peak corresponds to the partial recombination of decomposed groups to regenerate allophanate bonds. DSC curves recorded for original PUR confirm the conclusion — similar peaks are observed. For DSC cooling curve of coextruded PUR — PVC-U blend this peak disappeared. Perhaps during heating of this sample PVC reacts with decomposing allophanate groups products (Fig. 4).

IR spectra of the original PUR and recycled materials (Fig. 5) show similar characteristic peaks due to NH bond in urethane groups, C-H bonds in aliphatic chains and aromatic cycles, and C=O bonds. In the spectra of original PUR foams wastes the latter peak is divided into three peaks due to ester, urethane and allophanate groups. In the spectra of recycled materials only two strong C=O peaks are observed. The third peak corresponding to allophanate C=O bonds is the smallest one. Significant differences in characteristic IR peaks of original PUR samples and these of coextruded PUR — PVC-U blend were not observed.

Determination of solubility of PUR wastes confirms this product has partially cross-linked character — it is not soluble in dimethylformamid (DMF) and tetrahydrofuran (THF) while the PUR elastomer and PUR/PVC-U blends obtained in reactive extrusion are soluble in DMF and THF very well (Table 1). The average molecular weights of the extruded blends samples vary between 18 000 and 26 000.

T a b l e 1. Molecular weight of thermoplastic PUR elastomers obtained in reactive extrusion

Recycle type*)	Number average molecular weight (viscosity method) **)	Solubility in DMF/THF
PUR wastes	—	Partial/no
PUR 0	26 300	Good/good
PUR 5	19 200	Good/good
PUR 10	21 300	Good/good
PUR 15	18 500	Good/good

*) Numbers after the PUR symbol mark extruded blends with addition of respectively: 0, 5, 10 and 15 wt. % PVC-U.

**) Determined in dimethylformamid at 30°C [15].

The method of reactive extrusion proposed in this paper seems to be considerably cheaper than the known techniques of PUR utilization. It yields a thermoplastic granulate that can be injection molded or extruded giving various products. Good properties of the elastomer make it suitable material for various applications such as shoe soles, gaskets and hoses (oilproof ones), sheets or insulating films *etc.* The only limitation of the application is the color, which is practically exclusively black. Our method of twin screw extruder controlled degradation of PUR foams with degassing provides a product of strength comparable to that of the original material. Its character is thermoplastic and it can be applied in all these fields where PUR elastomers are usually used. Hence, the method is a comparatively cheap way of converting difficult to handle wastes into useful thermoplastic elastomer.

We have also performed coextrusion tests involving PUR foam wastes and thermally stabilized unplasticized polyvinyl chloride (PVC-U). The addition of PVC-U does not worsen the extrusion parameters and makes easier the process of polymer extrudate pulling as well as its cutting into pellets. It also prevents granules from partial agglomeration by sticking together. The properties of products are depicted in Figs. 6 and 7. The tensile strength of PUR — PVC-U blends specimens does not practically change with increasing PVC-U content (Fig. 6a). The elongation at break, on the other hand, is considerable reduced (from 220% to *ca.* 60%) for the amount of PVC-U rising from 0 to 15 wt. % (Fig. 6b). The presence of the latter slightly improves the Shore hardness (Fig. 7a) and slightly reduces the abrasion resistance of blends (Fig. 7b).

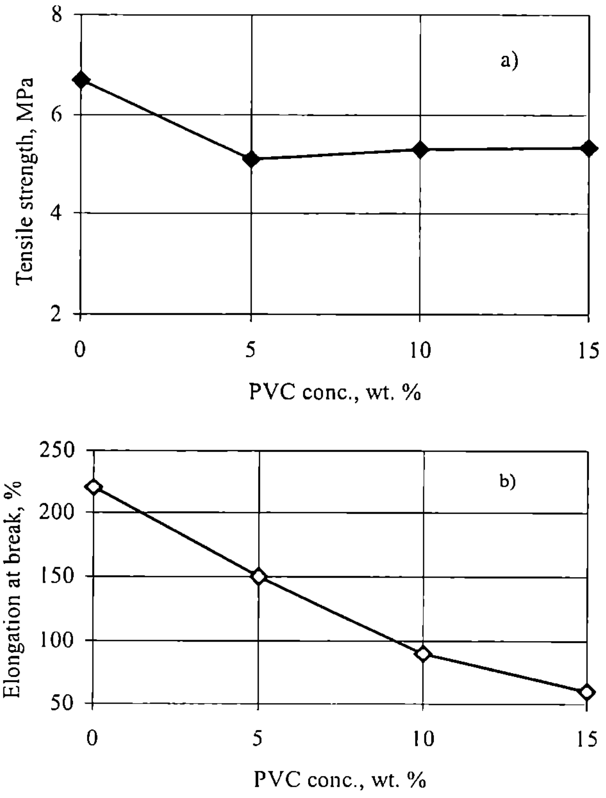

Fig. 6. Tensile strength (a) and elongation at break (b) vs. PVC-U concentration in the recycled PUR foams wastes

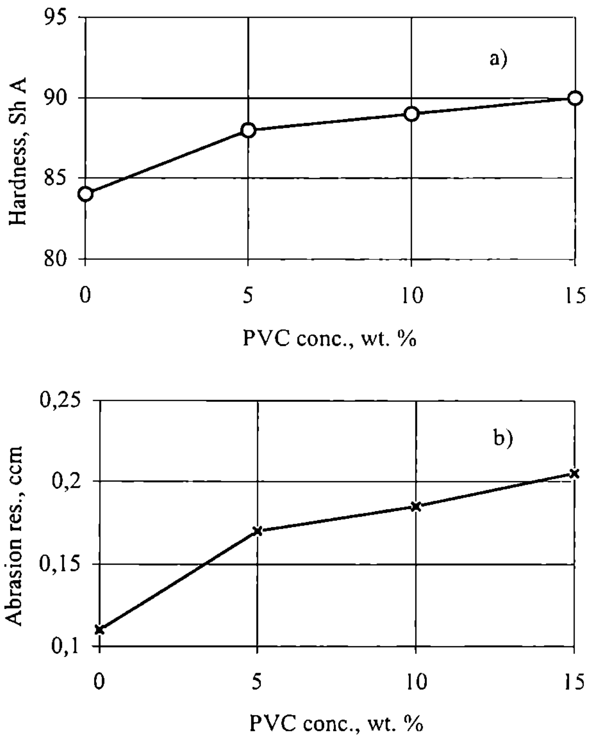

Fig. 7. Hardness (a) and abrasion (b) vs. PVC-U concentration in the recycled PUR foams wastes

From the data presented above the following conclusions could be drawn:

— Cast PUR wastes can conveniently be recycled to pelletized thermoplastic elastomer by reactive extrusion.

— Properties of the recycled elastomer are similar to those of the original cast PUR material.

— Reactive coextrusion of polyesterdiol based PUR wastes with PVC-U (5—10 wt. %) gives homogeneous polymer blends of improved hardness, slightly reduced abrasion resistance and strongly diminished elasticity.

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