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Solidification/stabilization of industrial wastes using polyurethanes

Summary — The results of solidification and stabilization of industrial wastes (metallurgical slag, lead smelting slag, flotation waste, scale), from various Polish factories, with using a polyurethane binder based on PMDI and one of following components containing OH groups: Rokopol G-1000, Terate 203 or water are reported. The effects of the type of a binder and its content as well as the type of waste on the density, hardness and compression strength of moldings of utilized wastes were investigated. It was stated that the type of a binder does not influence the properties investigated at a small range of binder content (up to 5.0 wt. %). From the economical point of view, using the PMDI/H_2O system as a binder is the most justified.
Key words: industrial wastes, polyurethane binder, solidification/stabilization process, utilized wastes properties.

Solid residues and wastes from the mining, metallurgical and chemical industries as well as from power stations are currently stored in slag, cinder dumps and landfills. Heavy metals, which are contained in the wastes, diffuse into the environment as a result of wind or leaching by rain. They contaminate the atmosphere as well as rivers and ground water. Thus, the development of technologies of safe treatment, handling and disposal of hazardous wastes is absolute necessity. But in spite of using the common methods like: reuse, recycling, incineration and land disposal, there are some residues, which must be utilized again.

The United States Environmental Protection Agency (EPA) [1] banned the disposal of hazardous wastes in landfills in 1985. So a development of solidification/stabilization technologies has begun as EPA has specified them as "best available technologies for a number of waste systems".

In the solidification/stabilization process, hazardous wastes are transformed into more compact, more chemically stable and less toxic forms, which can be used as prefabricated products for road construction and building [2]. These processes consist in adding certain types of materials to hazardous wastes to produce a new solid material [3]. The resulting waste form should be compact and mechanically strong (high compressive and flexural strength and good impact resistance), should have good water, weather and thermal resistances and be non-leachable.

A good binder system should detoxify and chemically fix hazardous and toxic components. Moreover, the binding rate (rate of fixation, solidification and stabilization) and waste loading should be high.

Polyurethanes based binder systems [4—6] are certainly among the most promising reactive binders because of their unique characteristics: a lot of possible chemical structures, ability of chemical fixation and detoxification, a very low degree of permeability, high binding rate and high waste loading.

The advantages of the solidification/stabilization using polyurethanes are the lack of by-products and the economy of the process.

Hitherto this technology was successfully used for utilization of wastes from life-end cars [7—9].

In this paper, we report the results of the solidification/stabilization of industrial waste from various Polish factories with using the binders based on polyurethanes. The effects of the type of a binder and a binder content on the mechanical properties of solidified/stabilized forms were studied. The studies were performed in cooperation with Polymer Institute, University of Detroit Mercy, USA.

EXPERIMENTAL

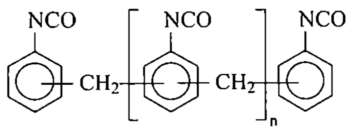
Materials

Binder components

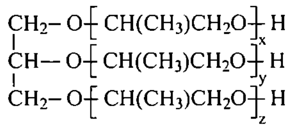
In the solidification/stabilization process, the following materials were used:

— polymeric MDI [PMDI, formula (I)] — Voronate M 220, Dow Chemical; NCO groups content 30—32%, viscosity at 25°C 180—260 mPa · s, Cl content max. 400 ppm, insolubles max. 0.1%;

— trifunctional polyether polyol [Rokopol G-1000, formula (II)] — Chem. Works Rokita, Brzeg Dolny, Poland; acid number max. 0.1, hydroxyl number 155—156, viscosity at 25°C 220—260 mPa · s, water content max. 0.1%;



(I)



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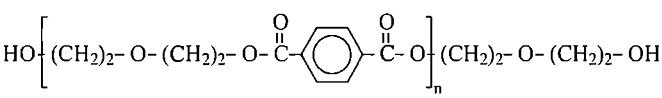

(III)

— aromatic polyester polyol [Terate 203, formula (III)] — Cape Industries; acid number max. 4, hydroxyl number 300—335, viscosity at 25°C max. 22 mPa · s, water content max. 0.1%, free diethylene glycol max. 11%.

Wastes

The binders based on the above mentioned materials were used for the solidification/stabilization of wastes listed below:

— scale containing: Fe (50—70%), SiO_2 (0.3—3.6%), mineral oils (1—11%), heavy metals (*ca.* 1.5%) from Metallurgical Works Lucchini,Warsaw, Poland;

— metallurgical slag containing, among others: Zn, Pb, Mg, Ca, Fe, Mn, As, Cd, S, Ag, C, SiO_2, Al_2O_3 from Metallurgical-Mining Works, Piekary Śląskie, Poland;

— lead smelting slag containing, among others: Na, K, Mn, Ca, SiO_2, Al_2O_3, As, S, Cl, Cu, Ag, Ni, Cd, Tl, Sb, Pb, Bi, Fe from Metallurgical-Mining Works, Piekary Śląskie, Poland;

— flotation waste containing, among others: Mg, Ca, SiO_2, Al_2O_3, C, As, S, Ag, Zn, Cd, Pb, Mn, Fe from Metallurgical-Mining Works, Piekary Śląskie, Poland.

Solidification/stabilization procedure

The solid waste was ground, dried at the temperature of 100°C for 2 hours and sieved by using a 1.25 mm sieve. Composites were prepared by adding, by turns, the specified amounts of Rokopol G-1000 and PMDI in the range of 2.5—15 wt. % of binder (Rokopol G-1000/PMDI weight ratio was 1:1) to the waste, followed by mixing and casting in preheated steel mould with internal dimensions of 5x5x5 cm. Then the samples were compression molded using hydraulic press at the temperature of 200°C under the pressure of 19.7 MPa for 3 minutes.

Some experiments were repeated at the Polymer Institute, University of Detroit Mercy, USA. The waste (scale) from Metallurgical Works Lucchini in Warsaw was cured with PMDI/Terate 203 binder (w/w = 1:1) at the temperature of 220°C under the pressure of 48.2 MPa for 3 min.

Properties of the moldings

The mechanical properties were measured according to the Polish standards:

— ball indentation hardness *H* (PN-93/C-89030/01), corresponding to ISO 2039-1973,

— compression strength σ_{SC} (PN-83/C-89031), corresponding to ISO 604-1973,

— density ρ (weight/volume ratio).

RESULTS AND DISCUSSION

The results of determination of mechanical properties of forms solidified/stabilized with PMDI/Rokopol G-1000 binder are presented in Table 1 and Figs. 1—3.

Table 1 shows that the increase in binder content in a scale does not influence the density of the final product. It results, however, in an increase in hardness (34% for the addition of 7.5 wt. % of the binder) and compression strength (42% for the addition of 10 wt. % of the binder). The values of hardness and compression strength are high even at smallest amounts of the binder (2.5%).

Table 1. Mechanical properties of moldings made of scale and PMDI/Rokopol G-1000 binder system

	Binder content, %			
	2.5	5.0	7.5	10
ρ, g/cm^3	3.7	3.9	3.8	3.8
H, MPa	202	257	271	264
σ_{sc}, MPa	57	67	72	81

The mechanical properties of moldings made of the same waste, but with the PMDI/Terate 203 binder (at the Polymer Institute, University of Detroit Mercy, USA) are similar.

Analogical studies were performed for the moldings made of metallurgical slag, lead smelting slag and flotation waste.

Density, hardness and compression strength of moldings made of the above wastes increase with an increasing binder content (Figs. 1—3).

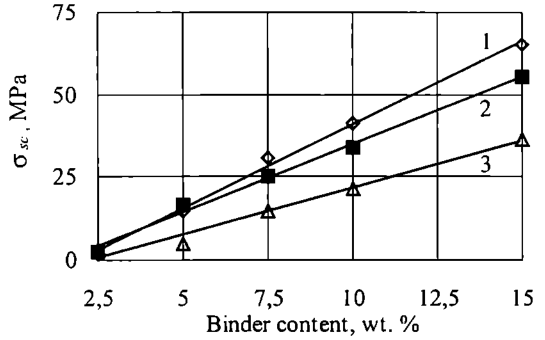

Fig. 1. Effect of binder content on the compression strength (σ_{sc}) of moldings made of PMDI/Rokopol G-1000 binder system and following wastes: 1 — metallurgical slag, 2 — lead-smelting slag, 3 — flotation waste

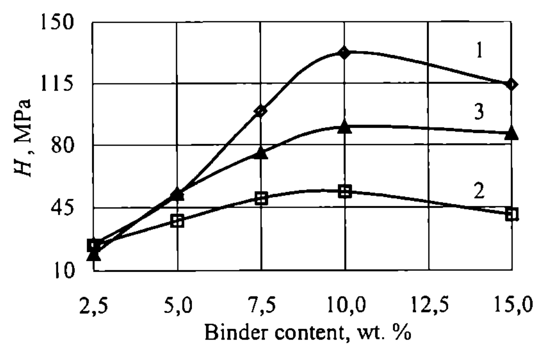

Fig. 2. Effect of binder content on hardness (H) of moldings made of PMDI/Rokopol G-1000 binder system and wastes; for symbols see Fig. 1

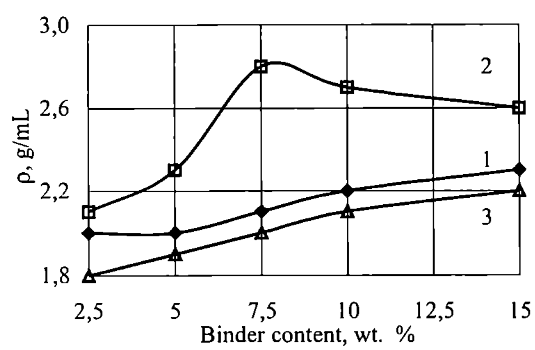

Fig. 3. Effect of binder content on density (ρ) of moldings made of PMDI/Rokopol G-1000 binder system and wastes; for symbols see Fig. 1

In general, it can be stated that the chemical structure of a binder and possible reactions of a component of the binder with a component at the surface of the inorganic particles do not affect the mechanical properties of the moldings. The binder/inorganic particles weight ratio, apart from the kind of waste, is the decisive factor here. Thus, the effect of a binder content on H and σ_{sc} seems to have a purely mechanistic character.

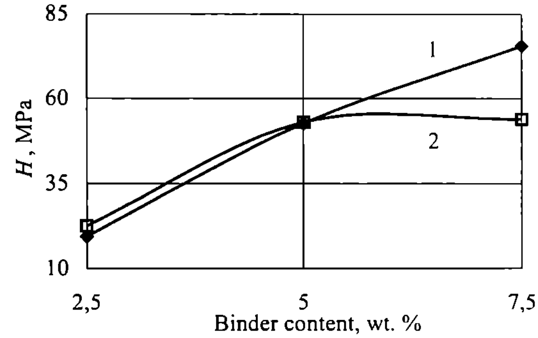

Fig. 4. Effect of binder content on hardness (H) of moldings made of flotation waste and binder system: 1 — PMDI/Rokopol G-1000, 2 — PMDI/ H_2O

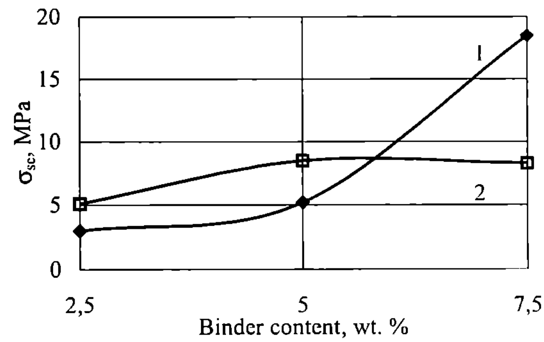

Fig. 5. Effect of binder content on compression strength (σ_{sc}) of moldings made of flotation waste and binder system; for symbols see Fig. 4

In order to reduce costs of the solidification/stabilization process, one component of the polymeric binder (Rokopol G-1000) was replaced by water. A comparison of H and σ_{sc} values of moldings made of floating waste and either PMDI/Rokopol G-1000 or PMDI/H_2O binders are presented in Figs. 4 and 5. Properties investigated are comparable for both types of binders in the range of amounts used: 2.5—5.0 wt. %. Moreover, inorganic salts were applied to better bind toxic heavy metals. Analysis of content of heavy metals in solutions after extraction of moldings with extraction fluids of various pH should show whether these metals would be better bound in moldings with addition of inorganic salts. The results of the analysis will be presented in the near future.

The mechanical properties of a series of moldings based on the flotation waste and PMDI/H_2O binder system (in the weight ratio 1:1, too) were determined. Hardness of the materials increases with an increasing binder content. The moldings prepared with an addition of 0.3% of disodium phosphate (Fig. 6, curve 2) exhibit the maximal hardness from among these materials studied.

The compression strength of the material considerably increases with an increase in the binder content (Fig. 7). At the amounts of the binder equal to 2.5 wt. %, the values of compression strength of moldings with

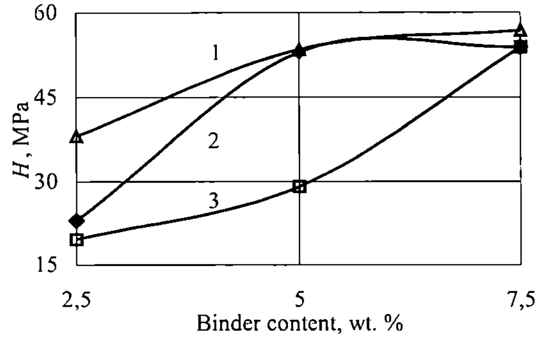

Fig. 6. Effect of binder content on hardness (H) of moldings made of flotation waste and PMDI/H_2O binder system with an addition of inorganic salts: 1 — without salt, 2 — 0.3% of disodium phosphate, 3 — 0.3% of sodium sulfate

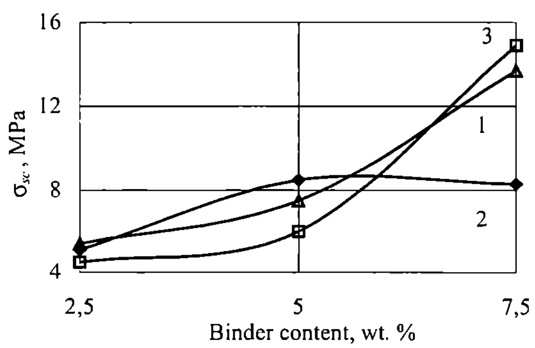

Fig. 7. Effect of binder content on compression strength (σ_{sc}) of moldings made of flotation waste and PMDI/H_2O binder system with an addition of inorganic salts; for symbols see Fig. 6

(curves 2 and 3) and without (curve 1) inorganic salts are comparable. At the binder content of 7.5 wt. %, σ_{sc} of forms made with addition of inorganic salts is considerably higher than that without salts.

It can be assumed that the effect of inorganic salts results from the catalytic activity of the salts on the isocyanate reactions with inorganic particles, water and polyols.

CONCLUSIONS

Polymeric isocyanate-based binder systems can be successfully used for the solidification/stabilization of industrial wastes. The process is economical due to the possibility of the low binder loading (even 2.5 wt. %). The efficiency of this binder system depends on the type of waste; moldings made of scale exhibit the highest mechanical strength (hardness and compression strength). These compact chemically stable and low-toxic moldings can be used as prefabricated products for road construction and building.

The use of the PMDI/H_2O binder system is more economical in comparison with PMDI/Rokopol G-1000 while the mechanical properties of moldings at useful amounts of the binder (2.5, 5 wt. %) are comparable.

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