Utilization of Polyethylene Waste and Polypropylene Wastes for Formation of Fine Copper Ore Concentrates

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Abstract. The possibilities for utilization of polyethylene waste and polypropylene waste as a binding material for formation of fine grain of copper ore concentrate in Hake Rheomix were examined. The optimum parameters of the formation processes were established. Strength, thermal and microscopic properties of the products obtained were determined.

1. Introduction
The most popular group of plastic materials are polyolefins. They are cheap and easily processed materials, which are excellent for various packing applications. That is why its share in the total amount of waste plastic materials approximates 60%. Usually, the thermoplastic materials are mechanically or thermally recycled. Every time, at temperatures above the pour point, the materials become plastic, without any change in chemical composition and in physical properties.

Due to considerable change in style of life, as observed in the last years, ecological impact of plastic waste materials, particularly single-trip containers, significantly increased [1-4], mainly in urbanized areas. In Poland, average family produces up to 370 kg of waste materials every year. It equals to the average for Europe, however, according to OECD sources, the average for the world equals to 490 kg per annum, [5].

This study was aimed at examination of the possibility for utilization of waste plastic material, polyethylene and polypropylene, as a binding agent for formation of briquettes of copper ore concentrate, which is used for smelting in shaft furnaces.

Generally, floatation concentrates of metal ores are briquetted with the use of inorganic binders, e.g. burnt lime, dolomite, magnesium oxide, cement, water-glass, etc. or with organic binders like, coal-tar pitch, asphalt, waste sulphite liquor or viscose for briquettes, [6-19]. In Poland, copper ore concentrates are formed with the use of sulphite liquor (Patent [20], Patent [21]). There are also many other ways for agglomeration or forming of copper concentrates (Patent [22], Patent [23], Patent [24], Patent [25], Patent [26]), except application of waste plastic materials.

2. Materials and methods of examination
Copper ore concentrate originated from the "Lubin" Mine, whereas polyethylene (PE) and polypropylene (PP) were used from a municipal waste dump. Concentrate and polymers were formed in the apparatus HAAKE RHEOMIX 600, described earlier [27].
First, the plastic material was melted in a mixer container, then bulk ore concentrate was added. Mixing at constant speed of 30 rpm was continued for a pre-determined period of time until a constant value of torque was reached. The tests were carried out within the temperature range of 20-220 °C, [28].

Samples of the product were thermally analysed in nitrogen atmosphere within the temperature range of 20-1000 °C. The sample heating rates were 10 °C/min and 40 °C/min, for DTA and DTG, respectively.

Dynamic properties (37 x 10 x 1-3 mm) of samples were determined by the DMTA method within the temperature range of 20-220 °C under standard amplitude of bending vibrations (1 Hz). The samples were formed by pressing of the copper concentrate and polymer-binder mixture under pressure of 5 MPa at temperature of 260 °C.

For examination of surface of the samples, a scanning electron microscope was used (JSM 5800 LV, manufactured by Jeol). The samples were covered with a coal film by vacuum sublimation. The microscope enabled the observation under enlargement up to a few dozen thousand times at resolution of 7 nm.

3. Discussion of the results
Composition of the mixture of copper ore concentrate and polyethylene/polypropylene binder was optimized taking into consideration the torque needed for mixing of the composites. Relations between composition and torque, as well as between torque and mixing time at a constant temperature are shown in Figures 1 and 2. The higher torque values, i.e. the higher viscosity, resulted from higher concentration of copper concentrate (85-90%). Stabilization of the torque value indications was the evidence of homogenization of the mixture.

Torque depends upon temperature of mixing [27]. The optimum temperature is 180 °C. At lower temperatures, mixing requires a much higher torque. Shares of polyethylene/polypropylene in the mixtures amounted to 10%, 15% and 20% by weight of the copper ore concentrate.

Thermal analysis proved that during heating the mixtures undergo an endothermic reaction of decomposition. In course of heating up the product comprising of 10% PE, formed at 180 °C, three endothermic peaks were observed. As observed from the TGA curve, the total loss of weight amounts to 27% and the process begins at 164 °C (Figure 4). It is assumed that this is the process of drying of the material. Decomposition of organic substances begins at a temperature of 450 °C and the maximum was observed within the temperature range of 472 and 477 °C.
Decomposition of organic constituents ends at temperature of 500 °C. Inorganic constituents of the composite decomposed at temperatures exceeding 772 °C (Figure 3).

Similar behaviour was displayed by composites of polypropylene. The product comprising 10% PP also gave three endothermic peaks. The total loss of weight amounted to 26% (Figure 6). The decomposition begun also at 164 °C, what may be the evidence that it is the moisture removal. Decomposition of organic binder begun at temperature of 420 °C and reached its maximum within the temperature range of 472 and 635 °C. Similarly to polyethylene composites, inorganic constituents decomposed at temperatures exceeding 770 °C (Figure 5).

Examination of mechanical strength proved that modulus of elasticity of the composites strongly depends upon composition of samples (Figures 7 and 8). Flow temperature, which amounts to 130 °C for pure PP, increases to 145 °C for the PE10% composite. In case of PP, the flow temperature increased from 130 °C for pure PP up to 180 °C for PP10% composite. The higher percentage of concentrate, the higher the flow temperature increase. Figures 9 and 10 show the relation between the vitrification and share of copper concentrate. It is accompanied by a noticeable increase of flow temperatures of the binders, from 130 °C for pure PE to 145 °C for 10%-composite, and from 130 °C to 180 °C for polypropylene binder (Figure 7, 8). It may be explained by excellent wettability of grains of copper ore concentrate by the polymers.

The tests proved that the best mechanical strength have the composites comprising possibly low amounts of binder (10% PE or 10% PP). Examination of polished sections, carried out with a scanning electron microscope enabled evaluation of structure of the composites and distribution of the binder. As seen from Figures 11b and 12b, the composites have a homogenous small-grained structure. An inorganic skeleton and an organic matrix of the binder in which the fines are dispersed can be
distinguished. Due to excellent wettability of ore with the binder, the composites are very well bound and homogenous.

**Figure 7.** Storage modulus for PE composite

**Figure 8.** Storage modulus for PP composite

**Figure 9.** Loss modulus for PE composite

**Figure 10.** Loss modulus for PP composite

The samples have an irregular texture and porosity of approx. 15% Figures 11 a), 12 a). Mineral constituents (copper sulphides, dolomite, etc.) occupy approx. Figures 11 b), 12 b) 40% of the total volume, the remainder being comprised of small grains combined with a binder, which is clearly visible in the contrast photographs, Figures 11 c), 12 c).
4. Conclusions
1. Positive results of the study create the possibility for utilization of polyethylene/polypropylene wastes, without any need for preliminary cleaning and removal of usual impurities.
2. The optimum composition of the product and optimum processing temperature has been determined by means of the Haake Rheomix 600 apparatus.
3. Both monitoring of mixing torque and results of analyses of the products obtained proved that:
   a) Mixing torque depends upon the share of the polyethylene or polypropylene binder in the copper concentrate composite. The lower the share the higher viscosity of the system and higher torque required for adequate mixing of the components.
   b) The best mechanical strength is observed in the samples comprising 10% wt. of the binder, processed at temperature of 180 °C.
   c) Components of the composites were uniformly distributed in the whole mass of the samples tested. Excellent products, having high mechanical strength, were obtained.
   d) Uniform distribution and suitable binding of components, resulting from good wettability of copper ore by the plastic material, were evidenced by microscopic examination.
   e) It has been found that irrespectively of the plastic type used (PE or PP), heating up to 1000 °C results in a comparable loss of mass and in endothermic reactions of decomposition. At lower temperatures, the composites have an excellent thermal stability, and decomposition of the binders begins above 400 °C. They are considered as having very good technical properties.

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