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Biomodification of plastic surfaces and depression process

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Plastics from the municipal waste must be recycled on a large scale. This contribution describes the initial work to determine the surface energy of plastic waste. Results of such investigations were correlated with both sedimentation and flotation data. The penetration rate of a liquid into the horizontal powder layer was measured; basing on the rate of liquid penetration, the effective radius of the porous bed was calculated. For modification of the surface of plastics, tannic acid, sodium lignin sulfonate and microbial broth from Pseudomonas aeruginosa growth were used. In order to determine the effect of these reagents on the surface energy of plastic powders, the penetration and flotation experiments were carried out. For polystyrene and polyethylene the estimated surface energy was 28.6 [mJ/m^2] and 24.5 [mJ/m^2], respectively. These results were correlated with the sediment height extreme of plastic powders in solvent pairs. The adsorption of tannic acid, sodium lignin sulfonate and biosurfactants from microbial filtrate caused an increase of the surface energy of plastic particles. For instance, the free energy of polyethylene particles was 34.9 [mJ/m^2] after the sodium lignin sulfonate treatment, and 35.57 [mJ/m^2] for the tannic acid adsorption. The natural flotation of plastic particles in the presence of modifying reagents was shown to be dependent on the concentration of these reagents.

1. INTRODUCTION

Conventional plastics are very difficult to decompose. According to the literature data, 75 billion pounds of plastics are produced every year in the United States [1], vast majority of them is collected in landfills. From the solid waste management point of view, plastic disposal is great problem, due to poor degradability - the decomposition process of plastics can take from 10 to 30 years. The composting of plastics causes only minor degradation [2,3]. Durability of this material is one of the qualities that makes plastic useful; however, its degradation (or biodegradation) proceeds very slowly. In a landfill, polystyrene (styrofoam) materials need 400 years and a plastic bottle 450 years for complete biodegradation.

A degree of plastics' recycling is very low (2%) in comparison with other materials, like aluminum (29%) or paper (21%). There are two main steps of plastics recycling: separation and purification. The most important for an efficient plastics' recycling are the initial steps of the process, i.e. selective collection and sorting.

This approach has the potential to create a new method of plastic waste separation. The general idea is to biomodify the surface of the plastics to affect their wettability, which will create the separation condition for the froth flotation. We are going to use the biomodification of plastic surface to change the surface properties. The mechanism of this biomodification is not well understood, but appears to be related to the plastic-bacteria interaction for a short period of time. Microorganisms are able to attach to plastic surface and colonize on it in a form of biofilm [4]. It is possible that biosurfactants and bioproducts produced by the microorganisms - similarly to synthetic surfactants - have an influence on the plastics floatability [5,6]. Adhesion of bacteria onto the mineral surface and their effect on mineral depression in anionic flotation has been investigated as well [7]. In this paper, we present the initial work undertaken to determine the surface energy of plastic materials and an effect of both chemical reagents and metabolic products on the plastics floatability. These investigations should be useful for the flotation-based separation of plastic waste.

2. MATERIALS AND METHODS

2.1. Materials

The sedimentation and thin-layer wicking experiments were performed with the following plastic powders: polystyrene, solid plastic waste and polyethylene. Polystyrene and polyethylene samples were purchased from POCh (Gliwice, Poland) as a pure granulate. The solid plastic wastes were derived from a municipal waste. Each of the samples was crushed in a special mill and screened. The 0.06–0.125 mm sieve size fraction was used for experiments.

Organic solvents used for sedimentation experiments were used as mixtures of nonpolar organic liquids. The liquid combination was chosen so that the surface tension of one liquid was lower than that of the second one. For the sedimentation experiments, n-hexane/hexadecane and n-hexane/cyclohexane pairs were chosen. The liquids were purchased from POCh (Gliwice, Poland).

Thin layer wicking experiments were carried out using typical liquids [8,9], namely n-heptane, hexadecane, formamide and double-distilled water.

The reagents used for selective depression: tannic acid and sodium lignin sulfonate, were purchased from Sigma-Aldrich Poland.

Pseudomonas aeruginosa bacteria were isolated from the soil samples. Cells were grown in 250 ml Erlenmeyer flasks containing 50 ml of liquid medium. Growth experiments were carried out with the medium composed of 20 g/l mannitole, 0.05 M NH_4NO_3, 0.03 M KH_2PO_4, 0.04 M Na_2HPO_4 $7H_2O$, 8 10^{-4} M $MgSO_4$, 7 10^{-6} M $CaCl_2$, 4 10^{-6} M Na_2EDTA, 10 mg/l $FeSO_4$ 7 H_2O. The chemicals were used as received without further purification. The strain was cultured in a rotary shaker (100 rpm) at room temperature. It is highly probable that biosurfactants produced by *P. aeruginosa* are mostly rhamnolipids of various structure.

2.2. Sedimentation experiments

For the sedimentation experiments, the glass vessel with graduated microtube was used. This vessel was used for the sediment column structure investigations [10]. The microtube was filled up by the sedimentation liquid then the plastic dispersion was prepared in the upper part of vessel. The selected liquid mixtures were used for the suspension preparation. When the polymer powder was totally homogeneous and wetted by liquid, the vessel was turn over and the plastic particles began to fall down into the microtube. After 12 hours, the sediment height of the plastic powder was measured. The results were analysed in terms of van der Waals interactions and mechanisms of particles aggregation [11].

2.3. Wicking method

Contact angle of the powder sample has been measured by means of the thin-layer wicking method [8,9]. The powdered plastic samples were deposited on a microscopic glass slide in the form of aqueous slurry. After drying the sample, one end of glass slide was connected with a liquid by transmitting wick; the liquid started to creep up the slide. The penetrating front of liquid was observed. On the glass cover of the chamber 1-cm sections were marked, and the times at the particular distances were recorded. At such basis the velocity of creep can be calculated. All measurements were made at room temperature. For the penetration experiments, n-heptane, hexadecane, formamide and water were used.

2.4. Flotation tests

The microflotation tests were carried out in the Hallimond tube. The total sample weight was 1 gram. The nitrogen gas flow rate was 27 cm^3 per minute. The float and nonfloating fractions were collected, dried, and weighed in order to calculate the percentage of floated material. The particle size range of 0.4–0.5 mm was used in the experiments.

3. EXPERIMENTAL RESULTS

The application of froth flotation for the separation of mixtures of plastics from municipal waste streams was investigated by Alter [12]. The mechanism of plastic flotation should be similar to the mineral particles flotation. However, the inorganic minerals have a high surface energy, whereas that of plastics is low. The concept of the critical surface tension of wetting was demonstrated at the low-energy solids flotation [13]. This parameter can be characterized by the relative wettability of low energy solid surface. The estimation of the critical surface tension of wetting or the solid surface free energy was the first step for the flotation studies.

The sediment volume of solid particles in liquids of different surface tension (γ_L) has been used by Wojcik [10] to determine γ_c of solid. The liquids or mixture of liquids were chosen in that way, the interfacial tension gradually changed.

In the non-aqueous media, there is a strong correlation between van der Waals interactions of solid particles and surface tension. The zero-interaction can be achieved when the surface tension of the suspended liquid is equal to the particle surface tension. Thus, it was possible to estimate the surface energy of plastics. The results of sedimentation experiments are presented in Figure 1.

The surface tensions of liquid mixtures, for which the extrema occur, are summarized in Table 1. The extrema (minimum or maximum) of the sediment height, obtained for investigated plastic samples, depend on the polarity of liquid used. In the case of less polar liquids the extrema are maxima.

In order to determine the surface free energy of solids, the thin-layer wicking experiments were performed; they did yield linear plots of s^2 vs. t for untreated and treated plastic powders. In Figs. 2 and 3, a plot of s^2 vs. t is given for alkanes (n-heptane, hexadecane) and polar liquids (formamide, water) of untreated plastic samples.

For each plastic powder, the value of R in the Washburn equation was obtained from the plots of $2\eta s^2/t$ vs. γ_L. Such plots yield a straight line, the slope being equal to R. The effective pore radius was used for the contact angle determination for polar liquids. These values are listed in Table 2.

The purpose of a depressant is to make the surface of particles more hydrophilic. In the mineral flotation, the water-soluble reagents are used as depressants. Shen applied methylcellulose to enhance the flotation separation of plastic [14]. According to his results, the effect of depressants on the plastic floatability can be divided into three categories: depressed, intermediated and high one. The methylcellulose depressant was found to be not effective for such separation.

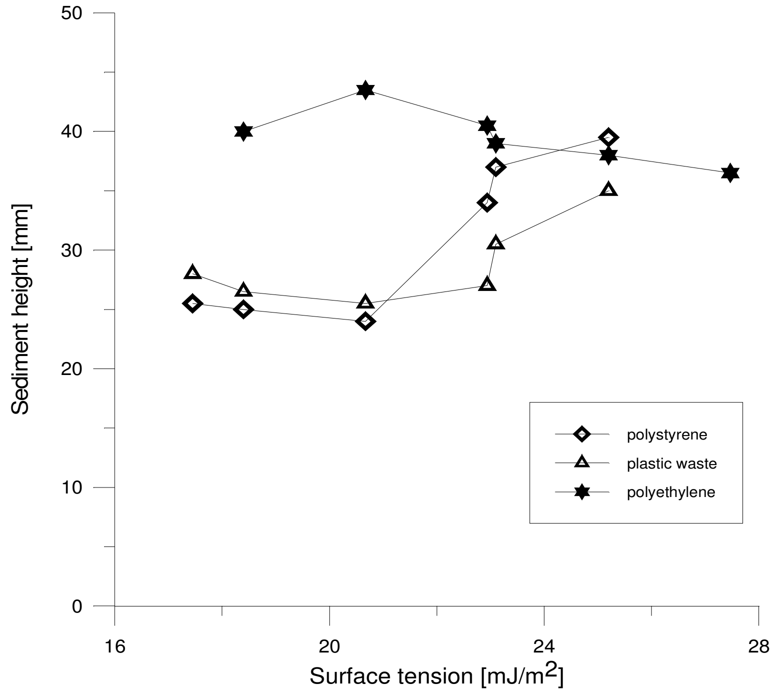

Fig. 1. Sediment height of plastic powders as a function of surface tension of liquid.

Tab. 1. Surface tension of liquid mixtures

Solvent pair	Material	γ extreme (mJ/m^2)
n-hexane/hexadecane	polystyrene	20.67 (max)
n-hexane/hexadecane	polyethylene	20.67 (max)
n-hexane/cyclohexane	plastic waste	20.7 (min)
n-hexane/cyclohexane	polystyrene	20.7 (min)
n-hexane/hexadecane	polystyrene and tannic acid	22.94 (max)
n-hexane/hexadecane	polyethylene and tannic acid	22.94 (max)
n-hexane/hexadecane	polyethylene and lignin sulfonate	22.94 (max)
n-hexane/hexadecane	polyethylene and lignin sulfonate	22.94 (max)

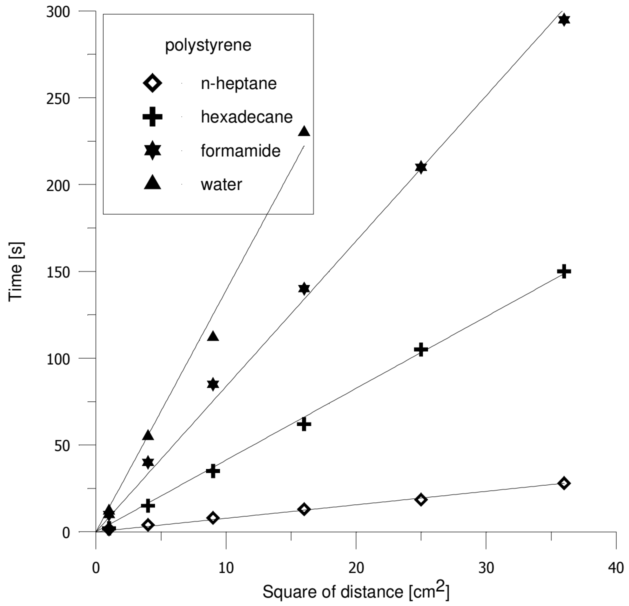

Fig. 2. Wetting of polystyrene powder by both apolar and polar liquids in TLW experiments.

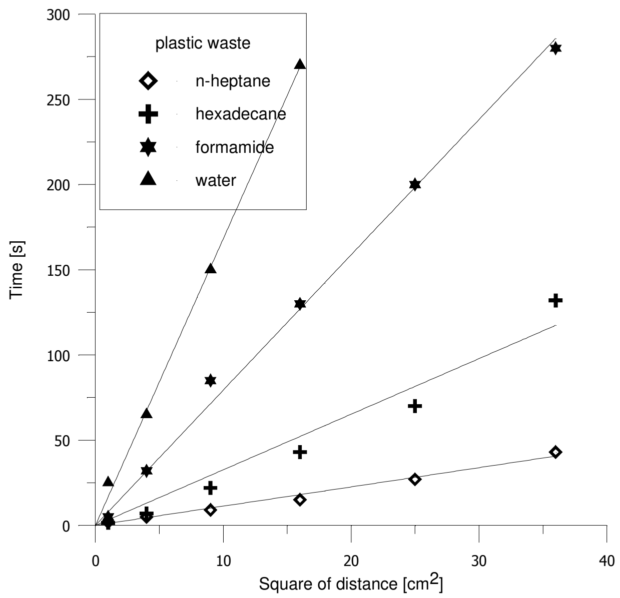

Fig. 3. Wetting of plastic waste powder by both apolar and polar liquids in TLW experiments.

Tab. 2. Effective radius R and apolar Lifshitz-van der Waals free energy components of plastic powders.

Material	Effective radius $R\cdot(10^5$ cm)	Free energy components γ^{LW}_s (mN/m)
Polystyrene	2.05	28.6
Plastic waste	5.84	24.5

For the selective flotation of many plastics the depressants, such as quebracho, tannic acid and poly(vinyl alcohol) were used. The quebracho and sodium carboxymethyl cellulose (NaCMC) were both found to be effective depressants of polystyrene (HIPS) and acrylonitrile butadiene styrene (ABS) [15]. At low pH quebracho depressed both ABS and HIPS.

The flotation tests, using calcium lignin sulfonate as depressant, showed that it was possible to separate poly(vinyl chloride) (PVC) from poly(ethylene terephthalate) (PET) [1].

According to the above results, we adapted the wicking technique to measure the surface energy of plastics, previously conditioned using both tannic acid and sodium lignin sulfonate solutions.

The modification of the plastic surface (polystyrene) with tannic acid or lignin sulfonate caused an increase of R value from $2.05\cdot10^{-5}$ cm to $3.17\cdot10^{-5}$ cm in the extreme case. The increase of this parameter may be considered in the terms of the adsorption of tannic acid and sodium lignin sulfonate on the plastic surface. The Lifshitz-van der Waals value of the solid free energy changed, because of the previous treatment process. For instance, the free energy of polyethylene particles after the sodium lignin sulfonate treatment was 34.9 [mJ/m^2] and 35.57 [mJ/m^2] for the tannic acid adsorption.

The plastic particles are hydrophobic by nature and naturally floatable [16]. In such case, a collector does not have to be applied to make the solid surface hydrophobic. The contact angles of plastics in aqueous solutions were determined to be around 90^o [6], therefore it was necessary to use a suitable depressant to achieve selective separation. Consequently, the floatability of plastic particles can be dropped with both lignin sulfonate and tannic acid. Microflotation studies were initiated to determine the flotation recovery of plastic particles versus the concentration of depressant reagent. In all cases, when concentration of added depressant reagent increased, the plastic particles become less hydrophobic. Figs. 6 and 7 present the results of plastic flotation recovery using depressant reagents (lignin sulfonate and tannic acid).

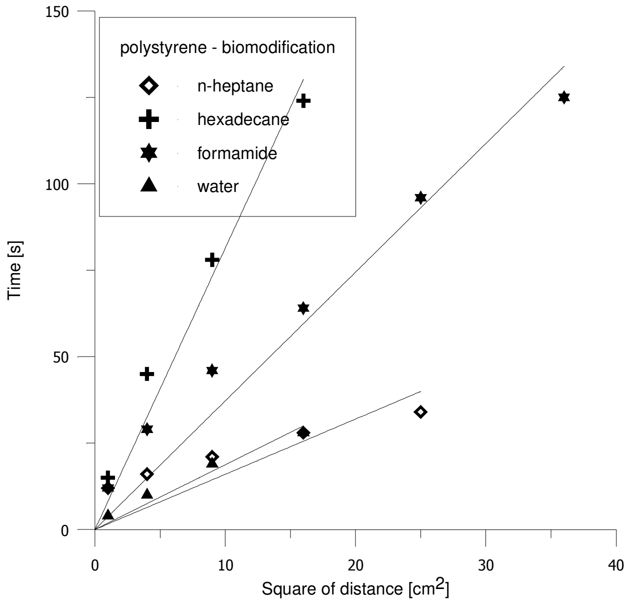

Fig. 4. Wetting of polystyrene powders after biomodification of the plastic surface.

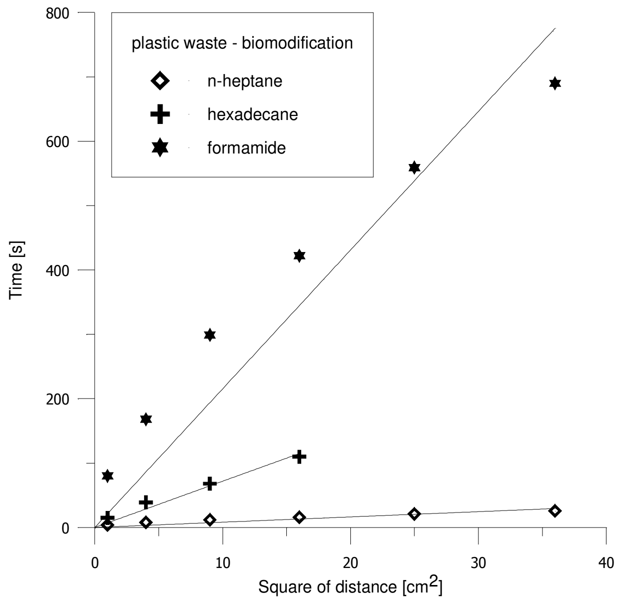

Fig. 5. Wetting of plastic waste powders after biomodification of the plastic surface.

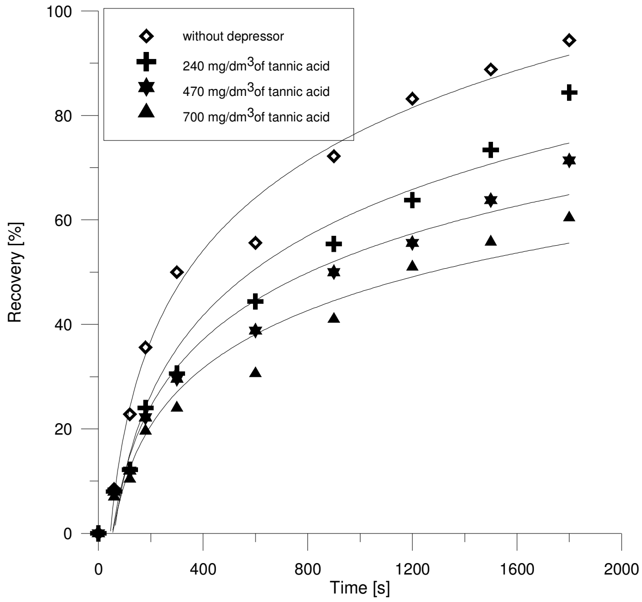

Fig. 6. Flotation recovery as a function of tannic acid dosage.

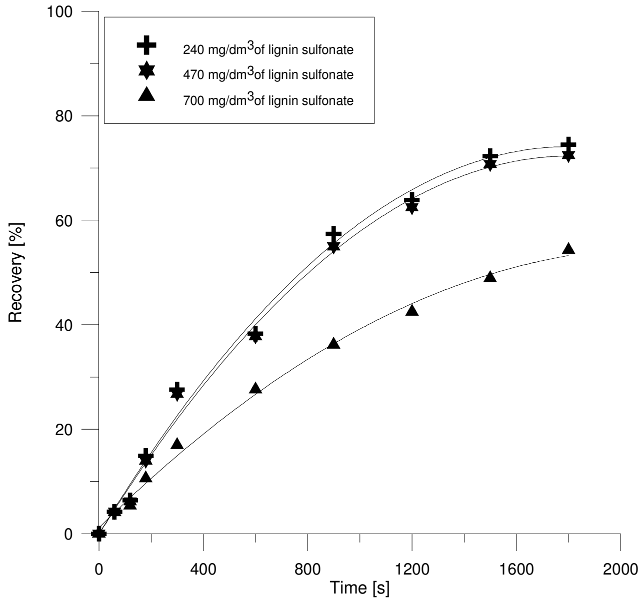

Fig. 7. Flotation recovery as a function of lignin sulfonate dosage.

Similar effects of biomodification were observed during the flotation, when the bacterial filtrate was used as depressant. It contains microbial cells and metabolite products, such as biopolymers and biosurfactants. It is possible, that these organic components or microorganism's cells, when adsorbed onto the plastic surface, influence the properties of surface. Therefore, the biomodification of plastic surface depend on the broth concentration.

The flotation recovery of plastics as a function of the broth addition is shown in Fig. 8. From this plot it can be seen that the plastic recovery generally decreases with the broth addition. Finally, the addition of 50 % of broth solution gives low flotation recovery of plastic particles.

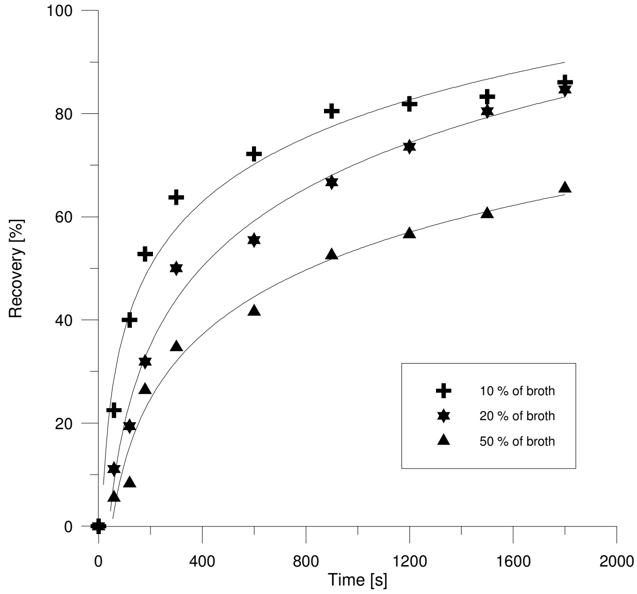

Fig. 8. Flotation recovery as a function of microbial broth amount.

The initial flotation tests supported the supposition that biopolymers and biosurfactants will affect the flotation process behaviour of plastic particles. Microorganisms are able to produce low and high molecular weight bioreagents [17]. The potential for selective flotation of plastics depends on the composition of microbial filtrate. The adhesion of selected microbial cells on the plastic surface and biomodification may be efficiently employed to the plastics separation processes.

4. CONCLUSION

The effect of modification of plastic surface was studied by the surface free energy determination. On the basis of the experimental results, the following conclusions may be drawn:

1. The sedimentation and thin-layer wicking methods adapted to the plastic powders appear to be very useful for the surface energy components determination.
2. The surface tension of the liquid mixtures, at which the extrema occurred, corresponded to the surface energy.
3. The adsorption of both tannic acid and lignin sulfonate affects the recovery of plastic flotation. The changes may be attributed to the surface energy increase.
4. A decrease of the plastic waste floatability in the presence of microbial broth is comparable to the depreciation, where other depressant reagents were used.

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