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A POSSIBILITY OF USING THE FLOTATION PROCESS TO SEPARATE PLASTICS

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ABSTRACT: Flotation is a physico-chemical process used traditionally to separate various solid materials, including plastics, based on a difference in their surface wettability. The surface of most plastics is hydrophobic which fact makes the selective flotation separation of target types of plastics from their mixtures with other types of plastic difficult or even impossible. To render the selectivity of the process itself, the surface of some plastics has to be selectively hydrophilized and so flotationally depressed. To make the surface of plastic selectively hydrophilic and thus nonfloatable, various methods have been tested such as adsorption of wetting agents or a physical treatment (flame, ozonization, plasma, photocatalytic, etc.). However, a potential of selective chemical treatment by incipient alkaline hydrolysis is recently emphasized, as exemplified by analyzing the surface hydrophilization of polyethylene terephthalate (PET) submerged with polyvinylchloride (PVC) in NaOH solutions even at ambient temperature and for a very short period of time. Indeed, the NaOH-pretreatment surface of PET foils was found to become hydrophilic (nonfloatable) to such an extent that flotation recovery and selectivity of PVC foils, whose surface was left almost untouched (and so entirely floatable) increased appreciably.

KEYWORDS: contact angle, contact angle hysteresis, flotation, recovery, wetting

❖ INTRODUCTION

Modification of solid surfaces is a very active field of research. On changing the surface composition, we obtain a material with new surface properties [Semal et al., 1999]. To make surface of plastic selectively hydrophilic and thus nonfloatable, various methods have been tested such as adsorption of wetting agents [Pongstabodee et al., 2008] or a physical treatment (flame, ozonation, plasma treatment, photocatalytic) [Pascoe and O'Connell, 2003; Okuda et al., 2007].

One of the basic experiments for gathering information about surface properties of PET from the view of its flotation recycling is the measurement of contact angles of water drops on it. The contact angles allow a simple and yet effective evaluation of the hydrophobicity of a solid surface and are an important parameter in wet processing of solid substrates such as froth flotation [Chau et al., 2009].

Therefore the evaluation of contact angles θ of water on solid surfaces plays an important role in surface characterization. In principle, a given pure liquid on an ideal (flat, homogenous, isotropic, smooth and rigid) solid in the presence of a given environment should give a unique value of equilibrium contact angle θ_e as determined by Young's equation (Eq.1):

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta_e \quad (1),$$

where γ represents the interfacial (or surface) tension and the suffixes define the interface. However in practice, it is rare for such a unique value of θ_e to be observed [Shanahan and Bourgués, 1994]. A surface which meets all the requirements of the Young's equation is referred to as an ideal surface. However, most practical surfaces are non-ideal and the measurable contact angle values on such surfaces are referred to as the apparent contact angle θ_{app} . As a consequence this value is not unique but falls into a more or less wide interval between the advancing θ_a and the receding θ_r contact angle. The difference between them is called contact angle hysteresis (CAH) (Eq.2) [Chau et al., 2009].

$$\Delta\theta = \theta_a - \theta_r \quad (2)$$

Hysteresis of contact angle is due to deviations of surface from ideal conditions [Erbil et al., 1999]. Interest in CAH is stipulated by the fact that CAH governs the wetting properties of the solid surface to a large extent [Bormashenko et al., 2008].

In order to make the surface of PET water wettable and thus non-floatable, wetting agents have been considered previously to apply. However, it is recognized that the surface of PET can be hydrophilized even selectively by simply immersing it in sodium hydroxide solutions (alkaline hydrolysis) together with other plastics (e.g. PVC) of comparable inherent hydrophobicity for a short period of time. In fact, because the surface of PET is affected-hydrophilized by NaOH solutions much

more than that of other plastics, the floatability of PET is uniquely suppressed [Drelich et al., 1998; Sisol, 2006]. Hydrolysis of solid PET is even less prominent at temperatures below its glass-transition temperature ($T_g \sim 85^\circ\text{C}$), becoming supposedly very sensitive to morphological factors of the PET surface that accompany its incipient degradation. Hence, the effect of two most important factors of hydrolytic degradation, namely the temperature and concentration of the NaOH pretreatment solution (up to 60°C and 8 %, respectively), on the surface hydrophilicity of PET foils must be studied in parallel with the determination of their surface morphology [Škvarla et al., 2010].

The hydrophilicity of PET foils stimulated by the chemical pretreatment was evaluated by measuring contact angles on water drops. The morphology and surface roughness of these foils were evaluated by atomic force microscopy (AFM). Additionally, electrokinetic (streaming current) measurements of PET foils were carried out in order to elucidate the relation between the extent of hydrolysis, hydrophilicity and the morphology of PET surface.

❖ EXPERIMENTAL

SAMPLES PRETREATMENT. Samples of PET foils cut from post-consumer plastic bottles were used. The foil samples with the size of ca. 50×50 mm and without any preliminary cleaning procedure were immersed in a series of aqueous sodium hydroxide solutions with concentration of 0, 2, 4, 6 and 8 wt% NaOH at temperatures 20, 40 and 60°C and stirred continuously for the period of 20 minutes. The NaOH-treated samples were taken out of the bath, rinsed with a large amount of distilled water to remove the remaining NaOH and air dried at 35°C . The PET samples will be in the next text referred to as for example PET2/40 or PET4/60, meaning the PET surface pre-treated in 2 % NaOH at 40°C or in 4 % NaOH at 60°C (PET4/60), respectively.

CONTACT ANGLE GONIOMETRY. A sessile drop technique was used to measure the static advancing θ_a and the receding θ_r contact angles of small ($\sim 3 \mu\text{l}$) liquid drops on the PET foil samples in air. All of the measurements were carried out by the Krüss EasyDrop Contact Angle Measuring System, allowing the determination of shape and size of measured drops from their images. The evaluation of digitized video images and the calculation of contact angles were made with the Drop Shape Analysis (DSA1) software. The resulting contact angle values were obtained as averages of both left and right side contact angle of liquid drop. For each surface, contact angles were measured on a minimum of 10 randomly positioned drops and averaged. The variance in the contact angle values did not exceed 3 degrees. The water contact angle hysteresis (CAH) was determined using Eq.2.

AFM. The MultiMode8 AFM in the PeakForce QNM (Quantitative Nanomechanical Property Mapping) mode was used to visualize the nano-texture and to measure the nano-roughness of the PET surface at the scan size of $2 \mu\text{m}$.

ELECTROKINETICS (STREAMING CURRENT). The streaming current measurements were performed with the Anton-Paar electrokinetic analyzer SurPass using the Clamping Cell that allows flattening of bent PET samples. For each measurement, a pair of PET foil sample was separated by a spacer introducing a gap of approx. $100 \mu\text{m}$. 1 mM KCl solution was used as the background electrolyte and its pH was adjusted with 0.1 M HCl and 0.1 M NaOH, respectively.

FLOTATION EXPERIMENTS. PET and PVC particles cut from post consumer bottles were floated in laboratory cell DV-2 with volume of 1.5 liters. The particles of PET and PVC with the size of ca. 5×5 mm with total weight of 30 g in ratio 1:1 were used in flotation process. Before flotation plastics were pretreated in NaOH solutions with concentration 4 and 6 wt. % at temperature 60°C for the period of 30 minutes. Air flow was $0.015 \text{ l}\cdot\text{min}^{-1}$ and stirrer speed was 840 rpm. Flotation happened at temperature 20°C in water or water with frothing agent (PEG - polyethylene glycol) $40 \text{ mg}\cdot\text{l}^{-1}$ environments. Flotation time interval was 2 minutes after flotation both of the products were dried, separated (based on the color of used plastics), weight and was evaluated their flotation recovery into the individual products. For another flotation experiment samples of PET and PVC were pretreated in 4 % NaOH solution at 20, 40, 60 and 80°C for the period of 30 minutes. Other flotation conditions are the same as previous.

❖ RESULTS AND DISCUSSION

Wettability. Figure 1 shows advancing θ_a (a) and receding θ_r (b) water contact angles, as well as their hysteresis $\Delta\theta$ (c) on the PET foil samples. Apparently, as indicated by both (decreasing) θ_a and θ_r , an increase in the NaOH concentration as well as temperature of the pretreatment solution had caused a continuous hydrophilization of PET foils. Employing the SigmaPlot 11.0 software it has been found that all three θ_a -VS- C_{NaOH} dependences (obtained for three different temperatures) can be expressed with a very high fit goodness by the four-parameter sigmoid transition function (see the smooth lines in Fig.1a).

AFM. Figure 2 summarizes $2 \times 2 \mu\text{m}$ 3D AFM scans of the untreated PET at 20°C (PET0/20) (a), pre-treated in 2 % NaOH at 20°C (PET2/20) (b), 4 % NaOH at 20°C (PET4/20) (c), and in 8 % NaOH at 20°C (PET8/20) (d) PET surface. The surface (a) contains hills which may causes with some impurities from pretreatment in distilled water. Average value of roughness parameter (Ra) acquired from five randomly chose the smoothest area on sample (a) was 0.8898 nm. Ra parameters were 0.8474 nm (b), 0.9586 nm (c) and 2.004 nm (d). With increasing pretreatment simultaneously increased roughness of

samples. Apparently, the surface morphology becomes more and more complex when the NaOH concentration is increased with rare hills.

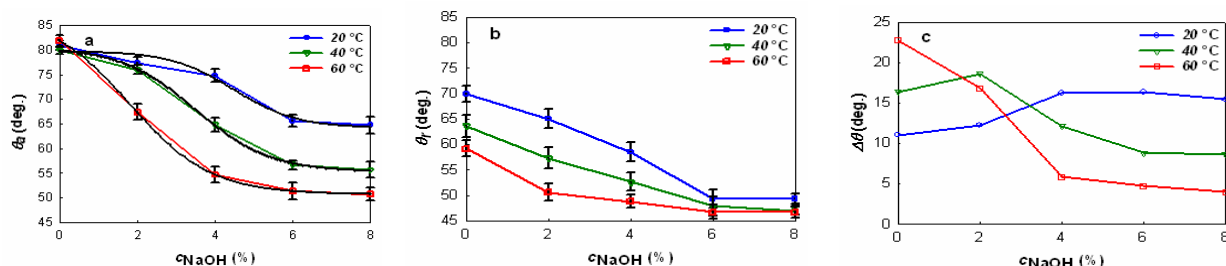


Figure 1. Advancing θ_a (a) and receding θ_r (b) contact angle and their hysteresis $\Delta\theta$ (c) of water drops on PET as a function of concentration of the NaOH solution at three different temperatures.

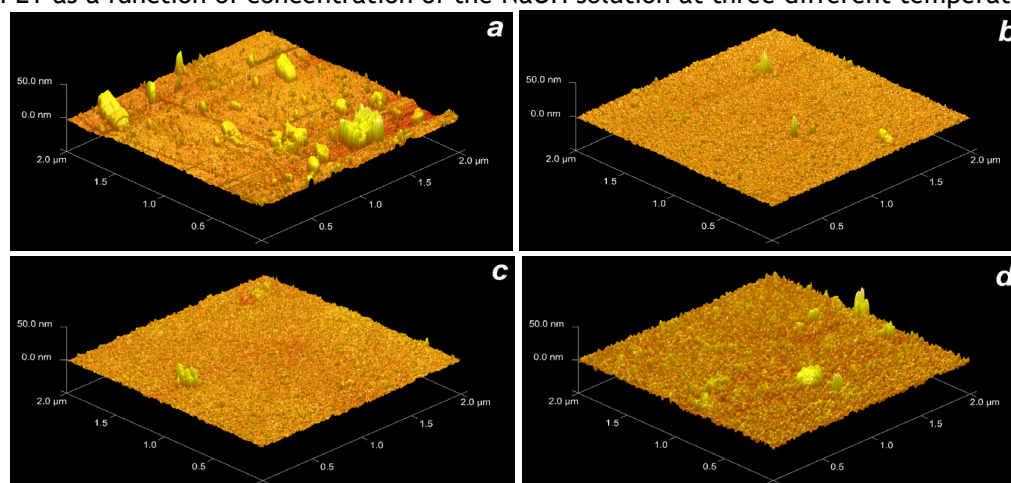


Figure 2. AFM images of untreated PET (a) and NaOH-modified PET2/20 (b), PET4/20 (c) and PET8/20 (d).

ZETA POTENTIAL. Figure 3 shows the ζ -potential of PET foils in 1 mM KCl as a function of pH.

With the increasing concentration (Figure 3a) as well as temperature (Figure 3b) of pre-treatment NaOH solution, all dependences ζ (mV)-vs-pH shift toward more negative values. Moreover, it is seen in both figures that there is a break point of all the dependences at pH 7 which can be ascribed to a change in the dissociation of functional groups at the PET surface. Interestingly, the ζ value at this pH for untreated PET is -53 mV. With the increasing PET pretreatment (rising the concentration of NaOH solutions at 40 °C) the ζ -potential grows even up to -100 mV in 4% NaOH but then decreases to -90 mV in 6% NaOH. Figure 4b reveals an analogous effect of temperature on the pretreated PET samples. Values of pH at which ζ -potential becomes zero (isoelectric point pIIEP) seem to vary unpredictably.

FLOTATION EXPERIMENTS. Picture 4a and 4b shows course of selective depress effect NaOH solution on PET at various temperatures. Picture presents clearly visible effects of increasing temperature plastic surface pretreatment to suppress PET flotability (hydrophilization). Already changed at 60 °C of treatment the recovery of PET to froth product to only 1.1 % and 100 % PVC. Hydrophobicity of the PVC after pretreatment in 4% NaOH remains unchanged to the extent that it is not necessary for its flotation and retention in the froth product used PEG as froth agent. Differences between the flotation with the addition of PEG concentration of 40 mg.l⁻¹ and flotation without the use are minimal.

Figures 4c and 4d depict the flotation results of PET and PVC. As seen from figure 4c high turbulence flotation environment caused by intensive stirring (840 rpm⁻¹) and structure used flotation cell, causing a decrease of flotability PVC particles. Their flotation recovery reaches 85.4 and 87.9% for pretreatment at 4 and 6% NaOH solutions. Flotability of PET is not affected by turbulence flotation environment and reaches recovery into the froth product 2.5% at 4% NaOH solution and 1.2% at 6% solution of NaOH. Flotability decreasing of PVC caused by increased turbulence flotation environment

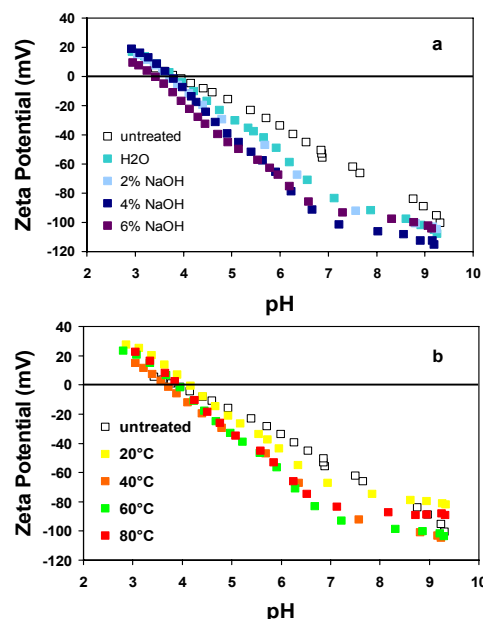


Figure 3. ζ -vs-pH dependences for PET foils pretreated in solutions of various (a) NaOH concentration (at 40 °C) and (b) temperature (2% NaOH)

was removed by adding PEG (Figure 4d). Froth agent created on the surface of the flotation environment strong and stabile froth, which prevented the particles fall out of PVC froth products due to turbulence and flotability of PVC, has increased to the value of 98.9 %. Addition of PEG did not affect significantly suppress flotability of PET.

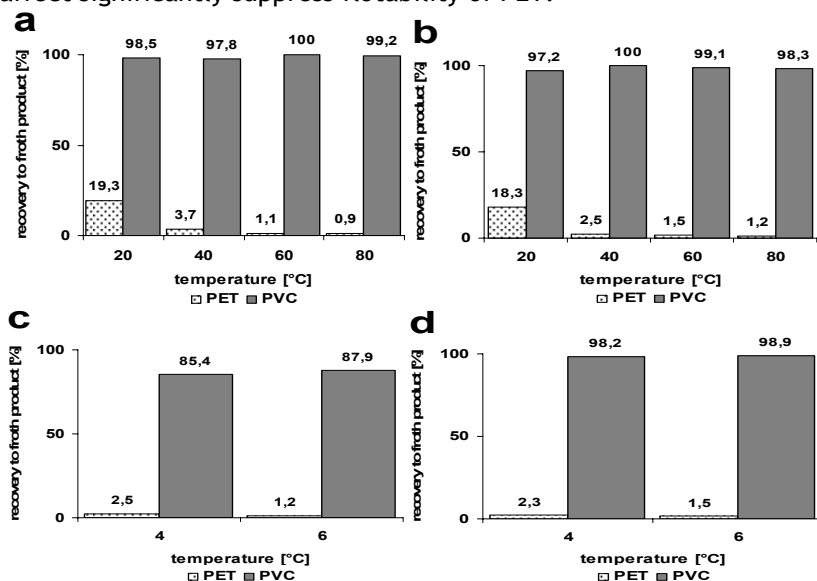


Figure 4. Dependence of flotation recovery of PET and PVC to froth product as a function of various temperatures of 4 % NaOH solution used for their pretreatment

together the hydrolytical attack and consequently the hydrophilization of PET foils. The sigmoidal shape of the relationships between the water contact angle values and the NaOH concentration, irrespective of temperature of the pretreatment solution, supposedly indicates an influence of the surface roughness on the hydrolysis kinetics. Indeed, the inflexion of these sigmoids is observed not only at the same NaOH concentrations for which the surface deterioration and dissolution but also the electric charges of PET surface were detected to be at maximum. So, the PET surface roughness is expected to fasten and slow down the reaction of hydrolysis at lower and higher NaOH concentration, respectively. Surface hydrophilization of PET and PVC plastic by alkaline hydrolysis demonstrated the decreasing of advancing and receding contact angles measured on these pre-treated plastic samples. Indeed, alkaline hydrolysis of the surface can improve the surface wettability of PET for the using of flotation separation of a mixture of PET/PVC, because PVC surface remains almost untouched after alkaline hydrolysis pretreatment. The flotation experiments indicate that surface pretreatment by alkaline hydrolysis (NaOH solutions up to 6 % and at temperatures below 60 °C) is sufficient to create a sufficient difference in hydrophilization PET and PVC surfaces, which ultimately reflect the recovery values of separated components to froth products.

Flotation was conducted without (a) and with (b) addition of PEG. Dependence of flotation recovery of PET and PVC to froth product as a function of concentration of the 4 and 6% NaOH solution at 60 °C. Flotation was conducted without (c) and with (d) addition of PEG.

❖ CONCLUSIONS

Wettability of PET foils evaluated by contact angle measurements is enhanced after their pretreatment in NaOH solutions at concentrations up to 6 % and temperatures up to 60 °C. Therefore, both the NaOH concentration and temperature are important factors of pretreatment, stimulating

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