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EVALUATING THE WETTING (SURFACE POLARITY) AND ROUGHNESS OF PET FOILS SURFACE DEGRADED BY INCIPIENT ALKALINE HYDROLYSIS

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ABSTRACT: One of the ways to weaken the inherently hydrophobic surface of plastics from the view of flotation separation is the application of alkaline hydrolysis. A pretreatment in NaOH solutions at low temperatures and/or concentrations of up to 60 °C and 8 %, respectively, for 20 minutes has been found to be efficient to decrease the surface hydrophobicity of PET foils to such an extent that their flotation ability is entirely depressed. Such a hydrophilization pretreatment also stimulates the PET's surface roughness, wetting of the surface and the thermodynamic equilibrium conditions at the surface and ultimately changes surface charge (polarity).

KEYWORDS: PET, alkaline hydrolysis degradation, wettability, interfacial free energy, contact angle measurements

❖ INTRODUCTION

One of the basic experiments for gathering information about surface properties of PET from the view of its flotation separation 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]. Moreover, contact angle measurements are still considered to be a relatively simple, useful, and sensitive tool for assessing the surface energy of solids, although this is not straightforward [Meiron et al., 2004]. However, interpretation of contact angles is not always straightforward because surfaces usually give two stable values, such that the contact angle at the advancing edge of a liquid drop is greater than angle at the receding edge. The difference between advancing and receding contact angle, θ_a and θ_r, is referred to as contact angle hysteresis (CAH) [Extrand and Kumagai, 1997].

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]. CAH is usually attributed to surface heterogeneity, roughness, overturning of molecular segments, at the surface, adsorption/desorption, interdiffusion, and/or surface deformation. With the exception of roughness and surface deformation, the other causes are physiochemical and have been implicitly assumed to be a contact liquid specific [Extrand and Kumagai, 1997].

It is well known that wetting of a surface by a liquid is affected by the roughness of the surface [Miller et al., 1996]. The main theoretical problem is the analysis of three-dimensional situations associated with rough or heterogeneous solid surface. In practice it is shown that not only the chemical properties (heterogeneity) but also mainly the physical properties (surface roughness, shape and particle size) of the surface influence its wetting behavior [Chau et al., 2009].

Modification of solid surfaces is a very active field of research. By changing the surface composition, we obtain a material with new surface properties [Semal et al., 1999]. In order to make the surface of PET water wettable and thus non-floatable, wetting agents have been considered previously be applied. 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].

Hydrolysis is the method of chemical recycling of PET by its reaction with water in acid, alkaline or neutral environment, leading to total depolymerization to its monomers (TPA and EG). The main disadvantage of this method is the use of high temperatures (200 - 250°*C*) and pressures (1.4 – 2 *MPa*) as well as the long time needed for complete depolymerization. Alkaline hydrolysis of PET is usually carried out with the use of an aqueous alkaline solution of NaOH or KOH, of a concentration of 4-20 *wt. %* [Karayannidis and Achilias, 2007; Carta et al., 2003; Paszun and Spychaj, 1997]. The alkaline hydrolysis reaction slows down significantly below its melting range (245 to 265°*C*), becoming a very complex process being limited by various physical factors such as diffusion, crystallinity, morphology, chain mobility, permeability, etc. Hydrolysis is therefore not widely used to recycle PET chemically in general. Moreover, it is also rarely used to produce food-grade recycled PET, because of the cost associated with purification of the recycled TPA [Karayannidis and Achilias, 2007].

Hydrolysis of solid PET is even less prominent at temperatures below its glass-transition temperature (Tg ~ 85°*C*) [Škvarla et al., 2010], 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.

In course of mildest alkaline hydrolysis wetting of the surface as well as surface roughness changes. The hydrophilicity of PET foils stimulated by the chemical pretreatment was evaluated by measuring contact angles on water drops and the contact angle values of drops of selected test liquids were used for the calculation of corresponding surface free and interfacial free energies at the PET/water interface. The morphology and surface roughness of these foils were evaluated by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Additionally, gravimetric 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*, 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 (~3 μl) 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 Equation 1:

$$\Delta\theta = \theta_{\mathrm{a}} - \theta_{\mathrm{r}} \tag{1}$$

In order to evaluate the surface free energy γ_S of PET samples, the Young-Dupré equation (Equation 2.) was adopted in the form derived from the Lifshitz-van der Waals/Lewis acid-base (LW-AB) surface thermodynamics theory, also known as the van Oss-Chaudhury-Good (VCG) model:

$$\gamma_{\mathrm{L}}(1+\cos\theta) = 2\sqrt{\gamma_{\mathrm{L}}^{\mathrm{LW}}\gamma_{\mathrm{S}}^{\mathrm{LW}}} + 2\left(\sqrt{\gamma_{\mathrm{L}}^{+}\gamma_{\mathrm{S}}^{-}} + \sqrt{\gamma_{\mathrm{L}}^{-}\gamma_{\mathrm{S}}^{+}}\right) \tag{2}$$

Advancing contact angles of two triplets of test liquids differing in the apolar liquid, namely α-bromonaphthalene-glycerol-water (B-G-W) and diodomethane-glycerol-water (D-G-W), were measured to determine γ_S and its components by using Equation 2. The PET/water interface free energy γ_{SL} is thus calculated from the Young equation (Equation 3):

$$\gamma_{\mathrm{S}} = \gamma_{\mathrm{SL}} + \gamma_{\mathrm{L}}\cos\theta_{\mathrm{L}} \qquad (3).$$

Atomic force microscopy (AFM)

The Nanosurf EasyScan Flex AFM in the dynamic mode with the NCLR cantilever was used to visualize the nano-texture and to measure the nano-roughness of the PET surface at the scan size of 2

μm. Samples of untreated and treated PET were analyzed on randomly selected positions all over the sample surface.

Gravimetry

The PET weight loss or gain in the course of hydrolytic reaction was determined at room temperature. For calculating PET weight conversion, the following equation (Equation 4.) was used:

$$C = \frac{m \times 100}{m_0} \quad (\%) \tag{4}$$

where m_0 and m refer, respectively, to the initial dry weight of (untreated) PET foils and the weight of the same PET foils periodically removed and dried at 35°*C* after immersing them in NaOH solutions of different concentrations at ambient temperature at increasing period of time.

❖ RESULTS AND DISCUSSION

Wettability

Figure 1 depicts 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. Effect of hydrophilization process increased by increasing concentration and temperature of NaOH solution. In course of the hydrophilization process, the surface of PET foils has become more wettable and rougher and change in PET surface charge occurs.

Advancing contact angle (θ_a) (Figure 1a) stays almost constant at all of three temperatures (20, 40 and 60°*C*) at neutral hydrolysis in distilled water. On the other hand receding contact angle (θ_r) (Figure 1b) decreases when temperature increases to 60°*C* at the same NaOH concentration. It appears that receding contact angles (θ_r) are difficult to be determined accurately because these contact angles are sensitive for changes on surface of PET foils cause by alkaline hydrolysis.

Measured values of advancing θ_a (a) and receding θ_r (b) water contact angles on untreated PET agree well with values measured by other authors. θ_a and θ_r were published to be 86° - 98° and 52°- 66° on PET plates cleaned in ethyl alcohol and then wiped with a piece of paper containing dilute soap solution and washed with distilled water. θ_a and θ_r were obtained by needle-syringe methods. θ_a = 71°- 88° were used as a comparison [Erbil et al., 1999]. Extruded polymer films of PET were cleaned thoroughly with acetone and ethyl alcohol and rinsed with a large amount of distilled water. θ_a was 84° and 83.5° in this study [Bormashenko et al., 2008]. PET (75 μm) films were used and pure uncross linked natural rubber. In this study θ_a was 71.0° [Extrand and Kumagai, 1997].

Figure 1a, b depicts that NaOH solution has distinct hydrophilization effect that proves decreasing advancing and receding contact angles values. Decreasing of both θ_a and θ_r is caused by not only increasing concentration of NaOH solution but also by increasing temperature of solution because the surface of PET foils is dissolving and becoming rough by NaOH pre-treatment solution. At high temperatures (40, 60°*C*) the decrease of θ_a and θ_r is even more distinct.

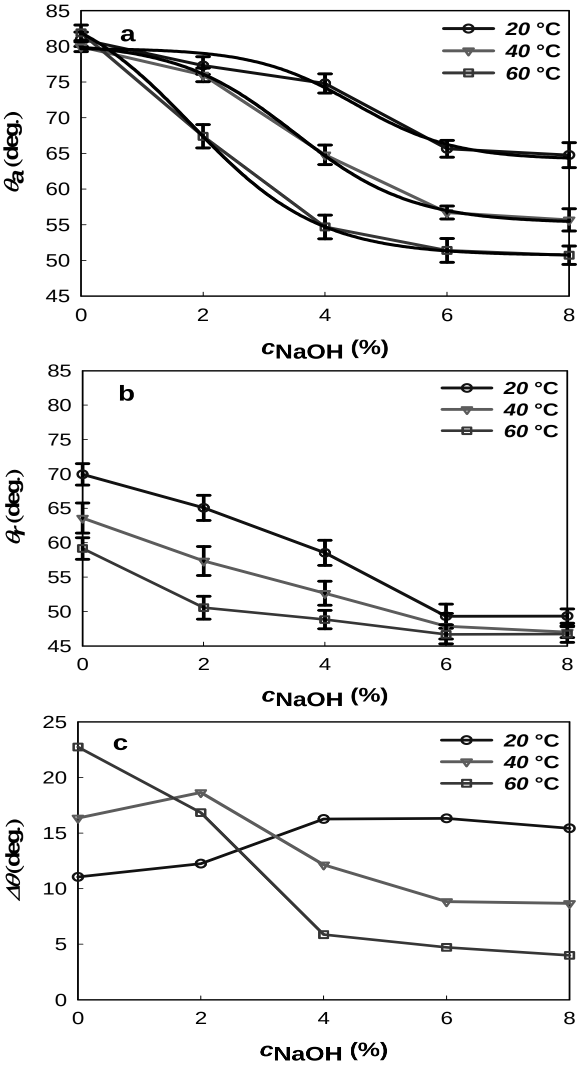

Figure 1. Advancing θ_a (a) and receding θ_r (b) contact angle and their hysteresis $\Delta\theta$ (c) of water drops on PET as a function of concentration of the NaOH solution at three different temperatures.

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 fourparameter sigmoid transition function despite of the limited number of experimental points (see the smooth lines in Figure1a).

Surface and interfacial free energy

Figure 2a and b depict the variation of interfacial tension γ_{SL}, calculated for the PET surface in contact with water, depending on the concentration and temperature of the NaOH pretreatment solution. The measurements were performed by triplets of test liquids: α-bromonaphthalene-glycerol-water (B-G-W) (a) and diodomethane-glycerol-water (D-G-W) (b). From Figure 2a and b can be seen that there is a decrease in the γ_{SL} from around 30 $mN.m^{-1}$ to $\approx$ 0 (corresponding to water $\theta_a \approx 50^\circ$), when hydrophilization of PET surface is at maximum (pretreated in 6 % NaOH at 60 °C). Nevertheless that used calculating theory allows negative values of γ_{SL} this method determined ultimately that γ_{SL} led to $\approx$ 0. It is difficult to determine why values of γ_{SL} at pretreatment in 8 % NaOH at 20, 40 and 60 °C almost always increase from minimal values. It can be associated with extreme dissolution of PET surface in NaOH solutions at highest concentration and especially at higher temperatures.

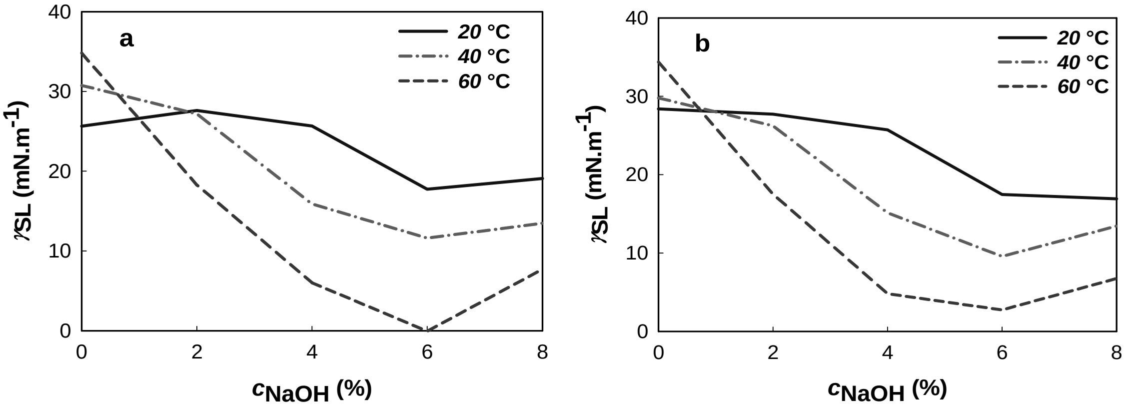

Figure 2. Free energy of the PET/water interface as a function of concentration of the NaOH solution at three different temperatures, calculated from contact angle data of B-G-W (a) and D-G-W (b) triplets of test liquids.

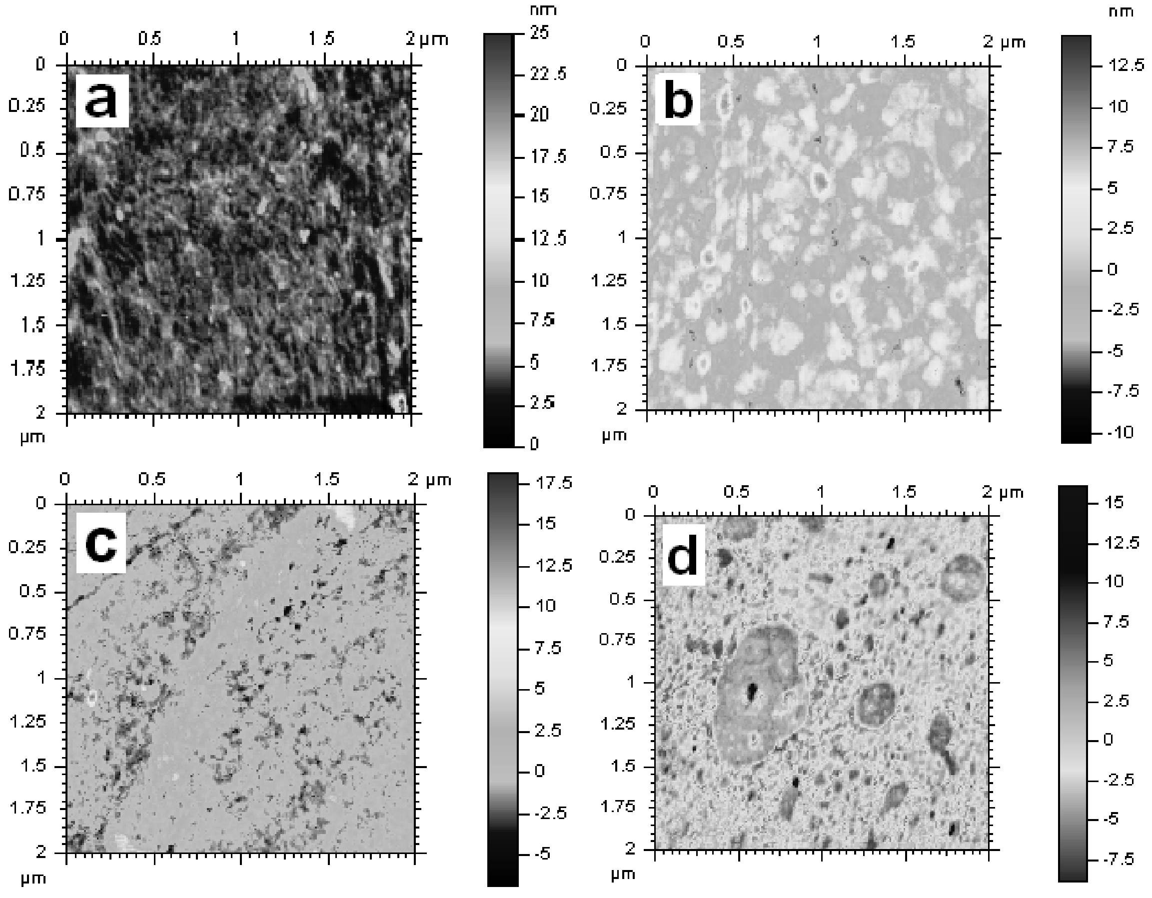

Figure 3. AFM images of untreated PET (a) and NaOH-modified PET2/40 (b), PET4/40 (c) and PET2/60 (d). The scan size: 2 × 2 μm.

Atomic force microscopy (AFM)

Figure 3 summarizes 2×2 μm AFM scans of the untreated (a), pre-treated in 2 % NaOH at 40°*C* (PET2/40) (b), 4 % NaOH at 40°*C* (PET4/40) (c), and in 2% NaOH at 60°*C* (PET2/60) (d) PET surface. The untreated surface is smooth and almost homogenous with sporadic and low elevations. Small hills and rare but deep cavities (pits) are visible on the surface of PET2/40. On the PET2/60 sample, islands of rounded shapes and different diameters surrounded with an array of pits can be seen. Apparently, the surface morphology becomes more and more complex when the NaOH concentration is increased. It should be mentioned however that the surface roughness on the above PET surfaces was found to attain a maximum for PET4/40 when more reliable 30×30 *μm* AFM scans were analyzed statistically (not shown here). In addition, from Figure 3d it is possible to make a statement about surface roughness of PET surface. Roughness is increasing with increasing NaOH concentration and temperature, whereas temperature seems more important than concentration of solution (PET2/60) Figure 3d.

Scanning electron microscopy (SEM)

Figure 4 complements the above AFM images that display the surface morphology of PET foils pretreated in NaOH solutions. Figure 4 presents the SEM images of a PET foil surface untreated (a) and pre-treated under relatively most drastic conditions, i.e. in 6 % NaOH solution at 60 °*C*, PET6/60 (b). It can be seen that the untreated surface looks very smooth while the pre-treated surface is rougher due to the partial hydrolysis. Moreover, on the pre-treated surface, small pits are distinguishable.

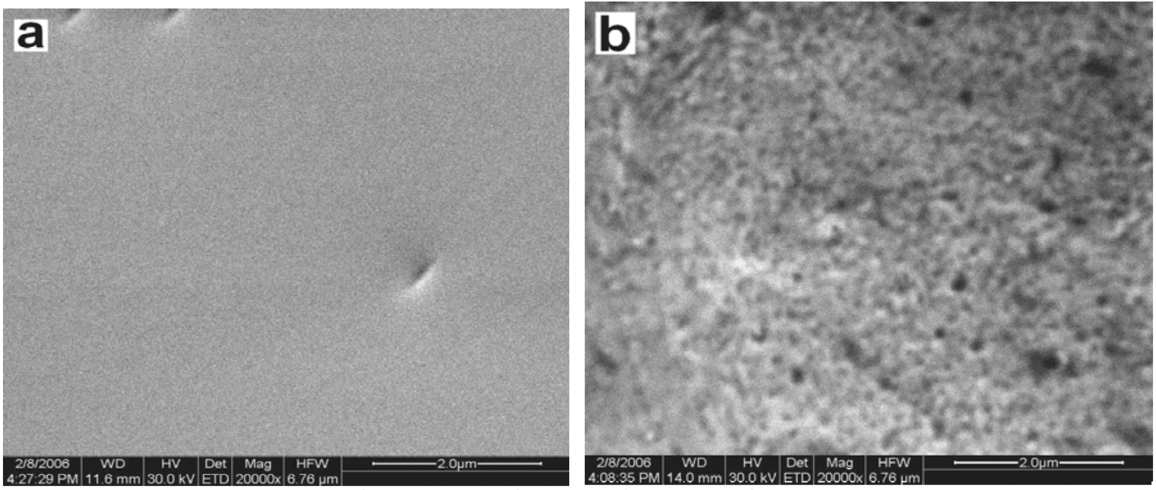

Figure 4. SEM images of untreated PET
(a) and NaOH-modified PET6/60 (b). Magnification: 20,000× (a, b).

Gravimetry

Figure 5 reveals that a weight loss of PET foils (calculated by Equation 4), after its immersion in the distilled water and NaOH solutions (2,4,6 and 8 %) at ambient temperature (20°*C*) for only 4 hours were negligible. But samples submerged in distilled water at 20°*C* (PET0/20) and 2 % NaOH at 20°*C* (PET2/20) for only 2 hours become heavier than before. This indicates that water from initial sorption was not removed from the PET surface after drying but must be overcome with the PET dissolution after a period of time (at ca. 4 *h*). Apparently, the sorption and dissolution processes are running parallel. Both the weight growth and the subsequent weight loss increase continuously with the addition of NaOH in the solution up to 8%. Throughout the whole process, the most extensive weight loss was observed at PET6/20 and PET8/20, which indicates that the surface of PET is markedly underlined by alkaline hydrolysis. Weight loss at PET0/20, PET2/20 and PET4/20 was increasing, but variable throughout the whole process.

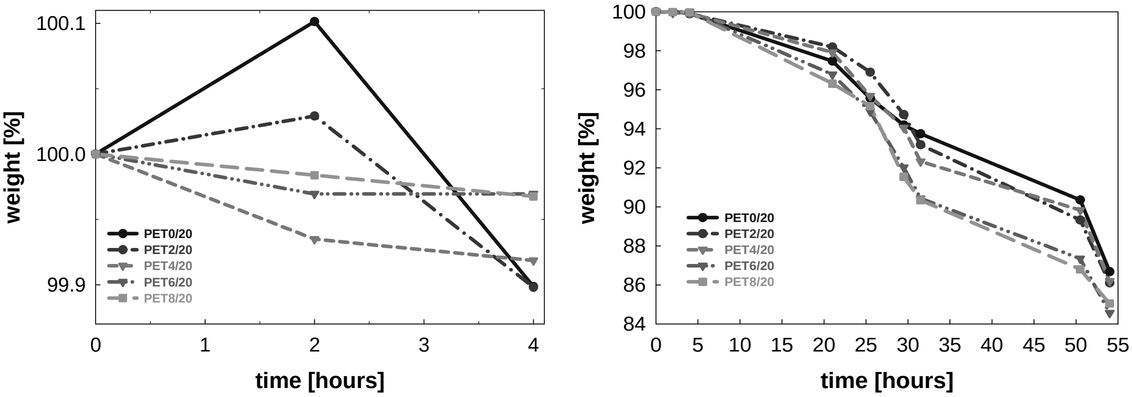

Figure 5. Weight changes of PET immersed in water, 2, 4, 6 and 8 % NaOH
at ambient temperature as a function of time.

❖ CONCLUSION

Wettability of PET foils evaluated by contact angle measurements is enhanced after their pretreatment in NaOH solutions at concentrations up to 8 % and temperatures up to 60 °C.

The concentration increased from 0 to 8 % NaOH and proportionally with them advancing (θa) and receding (θr) contact angles were decreased. Descending (θa), (θr) were 82.20° at 20 °C to 50.24° at 60 °C, 69.94° at 20 °C to 46.73° at 60 °C, respectively. Important factor of pretreatment was not only the concentration of NaOH solutions but also the temperature of solutions, which improved the hydrolytical effect and consequently the hydrophilization influence on PET foils. Hence surface of PET foils with hydropilicity is sufficient for flotation separation of PET from other hydrophobic plastics. Therefore, both the NaOH concentration and temperature are important factors of pretreatment, stimulating together the hydrolytical attack. 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 is highest but also the electric charge of PET surface was detected to be at maximum. So, the PET surface roughness is expected to speed up and slow down the reaction of hydrolysis at lower and higher NaOH concentration, respectively. But temperature seems to be more important factor than the concentration of solution which is shown at PET2/60 (Figure 3d). The calculation of interfacial free energies of the PET/water interface according to the LW-AB theory of wetting from contact angles of two test liquid triplets sets a thermodynamic limit of the PET hydrophilization pretreatment to occur in 6 % NaOH solution at 60 °C. Indeed, the decreasing value of γ_{SL} does not attain negative values (although it is allowed by the adopted LW-AB theory) for cNaOH above 6 % at 60 °C. The ζ-potential evaluated by the electrokinetic (streaming current) measurements complements and conductive to understanding processes in course of influence NaOH solutions on PET surface in mildest condition.

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