Free Energy Balance Of Polyamide, Polyester And Polypropylene Surfaces

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ABSTRACT
The wettability of a solid surface is often characterized by the contact angle of liquid on the solid surface. The wettability is pertinent to surface energy, which is an important parameter. The wettability can be affected, for example, by the roughness of the solid surface. In our work textiles are used as macroscopic roughness surfaces, and smooth plate surfaces are used as well to determine surface energies. For the calculation of surface energies it is fundamental to know the contact angle. The advancing and receding contact angles are measured, and the relation between the hysteresis and surface energy is monitored.

Keywords: advancing contact angle, receding contact angle, energy, contact angle hysteresis.

INTRODUCTION
When liquid contacts the surface of insoluble solids, three interphase energies are applied: interfacial energy between the solid and the gas γ_{sg}, interfacial energy between the solid and the liquid γ_{sl}, and interfacial energy between the liquid and the gas γ_{lg} whose relative values affect the final configuration of the system. If a drop of liquid is placed on the surface of a solid, the following results may ocur: if the surface energy of the solid is greater than the sum of surface energy of the liquid and interface energy of the solid - liquid, the liquid on the surface of the solid will spread in a continuous layer. Phase boundary solid - gas is replaced by the following interfaces: solid - liquid and liquid - gas. The resulting energy of the system is lower. The following is valid:

$$\gamma_{SG} > \gamma_{SL} + \gamma_{LG} \qquad (1)$$

A different result occurs when the surface energy of the solid is less than the sum of the interface energy of the solid - liquid and interface energy of the liquid - gas:

$$\gamma_{SG} < \gamma_{SL} + \gamma_{LG} \qquad (2)$$

In this case, a drop of liquid on the surface has a shape of equilibrium. This shape is characterized by the contact angle.

The relation of interfacial energies is known as the Young Eq. (1):

$$\gamma_{LG} \cdot \cos\theta = \gamma_{SG} - \gamma_{SL} \qquad (3)$$

The contact angle hysteresis can have an effect on the amount of energy and can be related to the concept of the energy barrier. The problem of the energy barrier was first introduced by Shuttleworth and Bailey [2] and discussed by Bikerman [3], Good [4], and Schwartz and Minor [5]. Johnson and Dettre [6] showed that the energy barrier was of utmost importance in determining hysteresis. For the first time, they computed the free energy barriers of an idealized rough surface with sinusoid shaped bumps and concluded that the actual values of advancing and receding contact angles depended on the barrier heights and vibrational state of the liquid drop. Subsequently, the concept of the energy barrier was further used in the studies of thermodynamics of contact angles. For example, Li and Neumann [7] used the concept of the energy barrier to discuss the effect of surface heterogeneity on contact angle hysteresis for a vertical plate with horizontal heterogeneous strips [8, 9]. They found that in the case of a low energy (high intrinsic angle) solid surface with an impurity of higher energy, the receding contact angles are less reproducible than the advancing contact angles. Lloyd and Connelly [10] made an attempt to directly measure energy barriers on rough and heterogeneous surfaces. Although the concept of the energy barrier is of utmost importance in determining hysteresis [6] and has found practical applications, existing theoretical studies on energy barriers are very limited. Most studies only discuss the effect of energy barriers on the contact angle. Quantitative results and discussion have been presented by only a few investigators, e.g. Johnson and Dettre [6] and Marmur [11]. Theoretical studies on energy barriers for rough, heterogeneous surfaces are too few. Long, et al studied contact angle hysteresis on rough, heterogeneous surfaces [12, 13]. They obtained advancing, receding and system equilibrium contact angles as a function of surface topography, roughness and heterogeneity. The role of energy barriers in determining various contact angle phenomena has certainly been explored.

J. Bico et al. described a model surface the different regimes of wetting of a rough surface exposed to a liquid. In this work they investigated how the surface roughness modifies the contact angle [14]. Similary, they studied the wetting of a solid textured by a designed roughness, the wetting of porous materials, and the conditions for observing such an imbibition and presented practical achievements, where the wetting properties of surface can be predicted and tuned by the design of a solid texture [15, 16].

Lee and Michielsen analyzed the behavior of wetting of a flat surface. This surface was compared with a rough surface, the effect of the sliding angles of water droplets, and the contact angle hysteresis on superhydrophobic surfaces. [17]. Further, they dealt with the preparation of a superhydrophobic surface [18].

Studies of the wettability and surface free energy are being assumed as important criteria for evaluation of adhesion properties of polymers. They are especially useful for the analysis of the effects of modification of the surface layer of polymeric materials. The wettability and surface free energy are of a great interest to scientists working in various fields of knowledge.

METHODS AND MATERIALS

Measurements of contact angles are among the most rapid and convenient methods of characterizing surfaces used in laboratories for this purpose. The sessile drop method was applied to measure the advancing and receding contact angles (see *Figure 1*). The contact angles were determined by optical method. A water drop on the material surface was observed under the microscope, and images captured with a digital camera (Canon PC 1032) were subsequently processed using software for image analysis, namely, LUCIA G (Laboratory Imaging Ltd., Czech Republic).

Before eash experiment, the surfaces of the materials were washed in distilled water and extracted with Dichloromethane G. R. stabilized (Lach – Ner). For the contact angle measurements, distilled water with a surface tension of 72.5±0.2 mN.m^{-1} at 20 °C was used. Individual measurements were performed on a new spot. A drop of water was placed on the material surface using a microsyringe. The advancing angle was measured after each volume increment (5 µl). The drop volume was increased up to 50 µl. The receding contact angle was measured after each removing of specific water volume (5 µl) from the drop up to 5 µl of the residual volume on the surface. The contact angles were measured 10 second after the application of the water drop on the material.

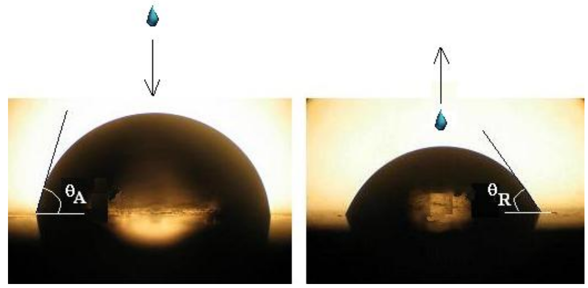

FIGURE 1. The advancing and receding contact angle.

A choice of a material for making a product is very important. This choice affects not only the product properties, but also the nature and course of the relevant technological process.

The chemical composition of a solid is one of the determining factors for the total amount of sorbing substances, and thus linked to its wetting. To study changes in contact angles, the following materials were selected: Polyamide 6.6, polyester and polypropylene (Silk&Progress). One of most important wettings systems is the wetting of textiles. In the case of textiles, wettability or water repellency is connected with the utility value of the textile structure. From a theoretical point of view, the textile structure is characterised by a large surface roughness and the periodic repetition of roughness.

In standard textile fabrics, contact angles could be affected, for example, by the yarn hairiness and yarn twist. Therefore, all fabrics used for measurements in this study were made from synthetic monofilaments with zero porosity in "yarn". Thus, absorption of water in to fabric structure is significantly reduced. This leads to simplification of monitored system in comparison with standard fabrics. For comparison, smooth plate from the same materials as the textiles was used. The smooth plates were prepared by melting and pressing of the relevant fabric samples (Department of Material, TUL). The description of the textile materials is given in *Table I.*

TABLE I. Description of the textile materials.

material	type of fabric	No. ends / No. picks [1/cm]	fiber diametre warp/weft [μm]
polyamide 6.6	woven	145/130	44/48
polyester	woven	62/62	55/80
polypropylene	knitted	-	103

RESULTS AND DISCUSSION

The water drop was deposited on both the smooth and textile surfaces. For calculation of surface energy, it is fundamental to know the contact angle. If a liquid drop is deposited onto a surface, it spreads. If additional liquid is added to the drop, the contact line advances and stops. Each time motion ceases, the drop exhibits an advancing contact angle θ_A. If liquid is removed from the drop, the contact angle decreases to receding value θ_R, and then the contact line recedes (*Figure* 1).

The advancing and receding contact angles for water drops were measured on both smooth and rough surfaces. When the volume of liquid changes, so does the length of the contact line. A liquid drop placed on the surface has a spherical segment shape. The experimental values of contact angles are presented in *Tables II - IV*. Values of contact angle hysteresis were determined from values of advancing and receding contact angles.

TABLE II. Contact angle values on smooth plate and textile surfaces for polyamide 6.6.

Volume [μl]	polyamide 6.6			
	smooth plate		textile	
	advancing angle	receding angle	advancing angle	receding angle
5	56.7	-	95.5	12.8
10	60.8	-	83.8	16.0
15	61.3	7.3	84.0	28.5
20	61.2	11.1	84.5	39.6
25	61.1	21.7	85.2	49.8
30	60.5	26.5	83.8	61.8
35	58.6	35.8	83.8	67.8
40	61.1	41.2	85.7	77.8
45	53.7	48.1	84.8	82.9
50	57.1	-	87.3	-

TABLE III. Contact angle values on smooth plate and textile surfaces for polyester.

Volume [μl]	polyester			
	smooth plate		textile	
	advancing angle	receding angle	advancing angle	receding angle
5	80.0	-	105.2	-
10	68.7	17.8	89.8	16.9
15	76.2	31.9	90.2	38.7
20	74.3	36.7	93.7	55.0
25	75.8	48.4	95.3	66.3
30	73.5	54.5	96.2	75.9
35	76.6	55.6	99.6	84.8
40	74.9	62.3	100.8	92.7
45	74.1	69.6	102.9	96.7
50	76.0	-	102.7	-

TABLE IV. Contact angle values on smooth plate and textile surfaces for polypropylene.

Volume [μl]	polypropylene			
	smooth plate		textile	
	advancing angle	receding angle	advancing angle	receding angle
5	95.3	16.7	126.1	32.5
10	77.4	41.1	117.5	45.0
15	75.9	36.5	115.2	75.9
20	79.5	39.3	116.2	86.9
25	80.7	45.1	126.8	94.7
30	75.9	49.2	127.0	107.2
35	77.1	53.2	121.4	114.2
40	78.5	60.4	119.4	119.9
45	76.3	69.5	118.6	121.7
50	78.9	-	122.6	-

To calculate the total energy we used the equations shown bellow. First, we determined the mass of liquid drop *w* according to Eq. (4):

$$w = \rho \cdot V \tag{4}$$

where ρ is density of liquid. For water the value 998.205 kg.m^3 at 20°C was used and *V* is volume of liquid.

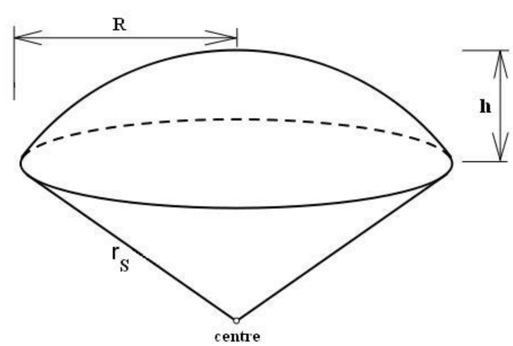

FIGURE 2: The spherical segment.

As shown in *Figure* 2, we define spherical segment height h from the values of contact angles θ and volume V according to Eq. (5):

$$h = \sqrt[3]{\frac{\frac{6 \cdot V}{\pi}}{\frac{3}{\left(tg\frac{\theta}{2}\right)^2 + 1}}} \tag{5}$$

The radius base of spherical segment R was determined according to Eq. (6):

$$R = \frac{h}{tg\frac{\theta}{2}} \tag{6}$$

These values (R and h) were used to calculated the radius of spherical segment r_s (see Eq. 7):

$$r_s = \frac{R^2 + h^2}{2 \cdot h} \tag{7}$$

Next, the height of the centre of gravity h_{CG} was determined from Eq. (8):

$$h_{CG} = \left(\frac{\left(\frac{3}{4} \cdot (2 \cdot r_s - h)^2\right)}{(3 \cdot r_s - h)} \right) - (r_s - h) \tag{8}$$

Equations for calculating the surface between the liquid and gas S_{LG} and surface between the solid and liquid S_{SL} are Eq. (9) and Eq. (10), respectively:

$$S_{LG} = 2 \cdot \pi \cdot r_s \cdot h \tag{9}$$

$$S_{SL} = \pi \cdot R^2 \tag{10}$$

Next we determined the pressure in the liquid drop p_{drop} Eq. (11):

$$p_{drop} = 2 \cdot \frac{\gamma_{LG}}{r_s} \tag{11}$$

To calculate the total energy, we also need to know the values of interfacial tensions, so we used Eq. (3). The value of interfacial tension gas - liquid is the table value for used liquid - in our approach it is distilled water of 72.75 $mN.m^{-1}$. Finally, the total energy was calculated according to Eq. (12):

$$E_{total} = E_{surface} + E_{potencial} + E_{pressure} \tag{12}$$

where:

$$E_{surface} = S_{LG} \cdot \gamma_{LG} + S_{SL} \cdot (\gamma_{SG} - \gamma_{SL}) \tag{13}$$

$$E_{potencial} = h_{CG} \cdot g \cdot w \tag{14}$$

where g is acceleration of gravity.

$$E_{pressure} = V \cdot p_{drop} \tag{15}$$

Figure 3. shows the values of energy for advancing and receding contact angles on smooth and rough surfaces of polyamide material. The results of energy balance of hysteresis on textile and smooth surface and their comparison are shown in *Figure 4*. The energy balance of hysteresis was calculated according to Eq. (16):

$$\Delta E = E_{total(A)} - E_{total(R)} \tag{16}$$

where $E_{total\,(A)}$ is energy for advancing contact angles, $E_{total\,(R)}$ is energy for and receding contact angles.

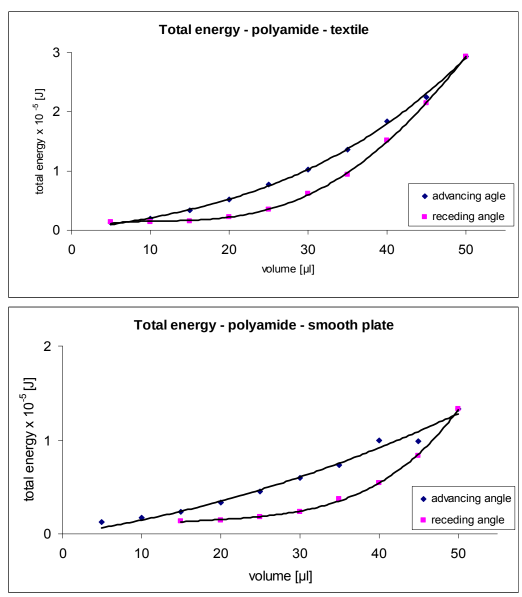

FIGURE 3. Comparison of total energy for smooth and textile surfaces of polyamide.

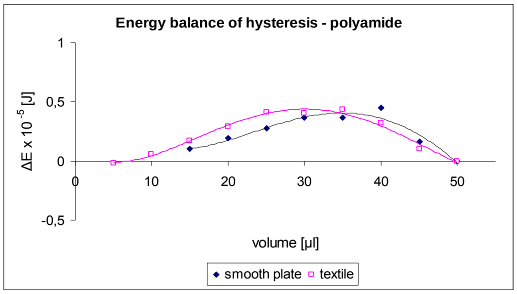

FIGURE 4. Energy balance of hysteresis on polyamide.

Similarly, in *Figure* 5 and *Figure* 7, the values of energy for advancing and receding contact angles on smooth and rough surfaces of polyester and polypropylene surfaces are shown. The results of energy balance of hysteresis on both textile and smooth surfaces are also shown in *Figure* 6. and *Figure* 8.

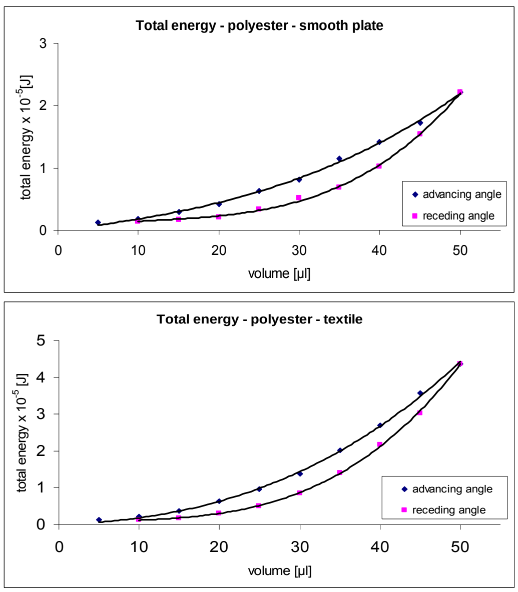

FIGURE 5. Comparison of total energy for smooth and textile surfaces on polyester.

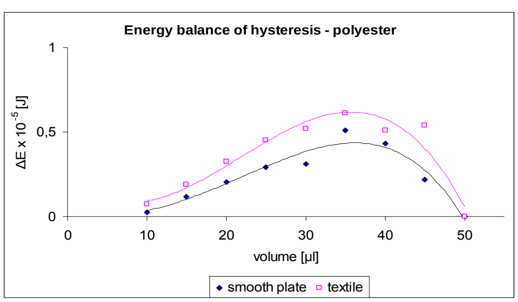

FIGURE 6. Energy balance of hysteresis on polyester.

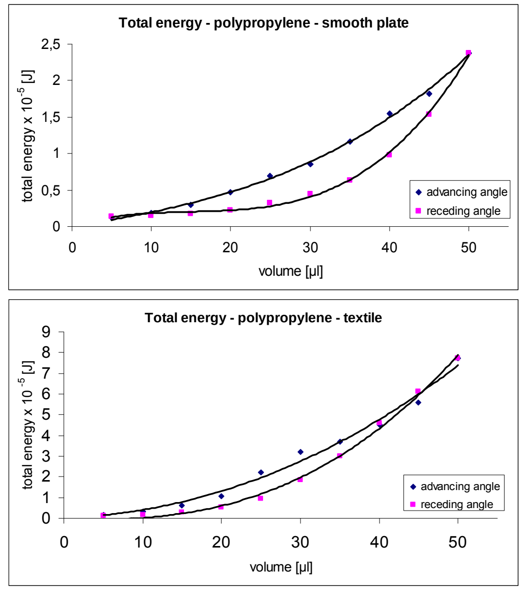

FIGURE 7. Comparison of total energy for smooth and textile surfaces on polypropylene.

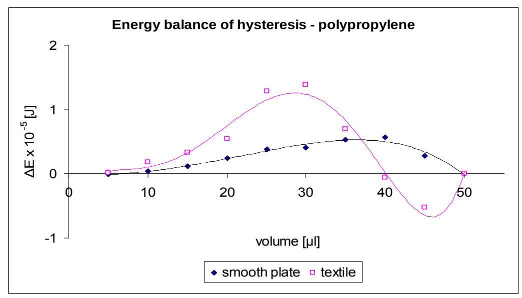

FIGURE 8. Energy balance of hysteresis on polypropylene.

We added an equal volume of water to drop up to the maximum value. When the volume increased, so did the value of total energy. In all runnings we can see that the energy increased.

When we removed water from the drop, the drop became smaller until the contact angle reached a minimum. In the case of the receding contact angles, the values of energy decreased as the contact angle decreased.

The results of energy balance of hysteresis show, that the total energy produced by all textile materials is more significant than that produced by smooth plates. The textile from polypropylene shown the highest values, on the contrary, the polyamide textile shown the lowest values of energy. The polyester presents transition between polyamide and polypropylene. As regards smooth plates, they have similar running of energy balance of hysteresis as textiles, but differences between individual kinds of materials are not so expressive.

The differences between individual used materials are in their properties. Polypropyne is watter-repellent, it has low offer of attractive forces for polar liquid as water is. In comparison with this, polyamide has higher low offer of attractive forces for polar liquids and more hydrophilic groups, therefore, values of contact angles are lower. Polyester stands somewhere between those two materials.

CONCLUSION

The contact angles of a liquid on a solid surface are represented by a range of values between two extremes: the advancing and the receding contact angles. On the textile and the smooth plate from polyamide 6.6, polyester and polypropylene, advancing and receding contact angles were measured. The values of differences between advancing and receding contact angles were determined as contact angle hysteresis. The contact angle hysteresis is important in understanding surface wettability and can be caused by the influence of surface roughness. After the contact angle hysteresis was measured the total surface free energy was determined.

From the results of energy balance of hysteresis it can be seen that there is a significant difference between the energy on smooth plates and textiles. The values of energy are lower for smooth plates from all used materials. The results in cases of textiles as rough surfaces, show opposite. There, the influence of air enclosed by a liquid drop probably makes itself felt in some extent. Therefore, the drop of water is formed on textile unlike on smooth plate. So, the contact angles and energies are higher.

A choice of a material for making a product is very important. This choice affects not only the product properties, but also the nature and course of the relevant technological process.

With the development and increasing scope of applications of polymeric materials and improvment of their functional properties in various areas of life, knowledge of wettability behavior and surface free energy has become increasingly more important.

Wettability is crucial for example to the production of composite materials, which play more and more of an important role in such vital areas as the automotive and aviation industries.

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