#### Marcela Bachurová, Jakub Wiener

Department of Textile Chemistry, Technical University of Liberec, Hálkova 6, 46117, Liberec, Czech Republic E-mail: m.bachurova@email.cz

#### Introduction

The contact angle is an important parameter for determining the measure of the hydrophobicity of surfaces. Contact angle measurements can be used in the calculation of solid surface tensions [1 - 3]. There exists numerous techniques [4 - 6] which can be used to measure the contact angle, most being based on Thomas Young's equation of 1805 [7]. Young's equation explains the equilibrium of the three interfacial tensions:

 $\gamma_{LG} \cdot \cos \theta = \gamma_{SG} - \gamma_{SL} \tag{1}$ 

where:

 $\gamma_{LG}$  is the interfacial energy between the liquid and gas,

#### Abstract

In our work we theoretically analysed the influence of textile structure on the hysteresis of wetting. The situation with current fabrics is complicated and the properties of fibers, yarns, and geometric arrangement also influence their wetting. The basis of the theoretical model is a simple plain weave fabric made from monofilaments. From this model we determined the real contact angle and apparent contact angle, and later we compared these values with results from the experimental measurement.

**Key words:** real contact angle, apparent contact angle, contact angle hysteresis, textile structure.

 $\gamma_{SG}$  the interfacial energy between the solid and gas,

 $\gamma_{SL}$  the interfacial energy between the solid and liquid, and

 $\theta$  is the Young contact angle.

Young's equation assumes that the solid surface is smooth, homogeneous and rigid and should also be chemically and physically inert with respect to the liquids to be employed. In a real system there is a range of contact angles between two extremes. The highest value of the range is the advancing contact angle  $\theta_A$ . The lowest value is the receding contact angle  $\theta_R$ . The difference between the advancing and receding contact angles is known as the contact angle hysteresis, H:

 $H = \theta_A - \theta_R \tag{2}$ 

Practically, all solid surfaces exhibit contact angle hysteresis, and because of which, the contact angle interpretation in terms of Young's equation is contentious. Although contact angle hysteresis has been studied extensively in the past several decades, the underlying causes and its origins are not completely understood [8]. Studies have attributed contact angle hysteresis to surface roughness [9 - 12] and heterogeneity [13 - 15], as well as to metastable surface energetic states [16-18]. Some found that the hysteresis decreases with the increasing molecular volume of the liquid on the monolayers [19]. In more recent studies, Schwartz and Garoff [20, 21] found that contact angle hysteresis is strongly dependent on the patch structure of the surface, whereas McCarthy and his co-workers [22, 23] related it to molecular mobility and packing as well as to the roughness of the surface in molecular dimensions [24].

The theory of determining contact angles on rough surfaces involves difficult conceptual and mathematical problems. This is especially true when rough surfaces are considered in three dimensions without any special symmetry. Since most practical surfaces are rough to some extent, these problems are very important for all real solid-liquid-fluid systems. The relationship between the intrinsic contact angle, which characterises mainly the interfacial material's properties, and the apparent contact angle, which should be a measurable parameter, is very important.

The intrinsic contact angle is that which a liquid would make with an ideal (i.e. rigid, flat, chemically homogeneous, insoluble and non-reactive) solid surface. In the absence of line tension effects or constraints [25, 26], it is equal to  $\theta$  - the contact angle predicted by the Young *Equation 1*.

Mainly, when observing the wettability of textile materials it is necessary to mention the apparent contact angle. Each contact angle whose size is related to other parameters of the surfaces tested, rather than the chemical composition, is a so-called apparent contact angle. The basic reason for this is complicated surface geometry and the non-homogeneity of the surface.

The apparent contact angle is that between the apparent solid surface and the tangent to the liquid-fluid interface [27]. This is connected with the determination of the contact angle. Gocławski presented a method of contact angle measurement for selected textile surfaces using a method based on the ADSA (Axisymmetric Drop Shape Analysis) numerical model [28]. Petrulyte and Baltakyte presented investigations into the wetting of terry fabrics, in which the process of liquid absorption was analysed from the moment of the drop falling onto the fabric's surface until it is absolutely absorbed by the material, and the spot being changeless [29]. Dembický and Wiener presented a simulation of single fibre wetting. The authors defined a stationary system composed of a fibre, liquid and air by a numerical method [30].

#### Theoretical part

The aim of this work is to analyse theoretically the influence of textile structure on the hysteresis of wetting. The situation with current fabric is complicated. The properties of fibres, yarns, and the geometric arrangement also influence its wetting. The wetting, and thus the contact angles measured on the fabric, is affected by various parameters such as twist and yarn hairiness. Current fabric is not completely describable, for it is complicated to define the wetting phenomenon.

The basis of the model is a simple plain weave fabric (*Figure 1*), where we can study different geometrical arrangements of the liquid on the idealised surface. In regard to the maximal simplification, fabric made from monofilaments is used for the theoretical model and experiments.

The model is based on the idea that the critical place, which determines the size limit of the apparent contact angle  $\beta$ , is the course of the highest placed monofilaments (curves  $S_1$  and  $S_2$  in *Figure 1*). This simplifies the situation, which can now be solved in a two-dimensional variant.

The spreading of the water drop on the surface of the fabric is evident from *Figures 2* and *3*. Based on the model there are two limit states, which correspond to the advancing (*Figure 2*) and receding (*Figure 3*) contact angles.

The limit for the advancing contact angle is given thus: that the next shift of the contact point of the liquid on monofilament that is away from the center drop



*Figure 1.* Structure of yarn interlacing with used fabric made from monofilament.

would lead to crossing the barrier formed by the perpendicular monofilament.

The limit for the receding contact angle – the reduction of the liquid volume would lead to crossing the barrier toward the center of the drop.

In this system the real contact angle  $\alpha$  is applied, which corresponds to the contact angle measured under the same conditions as on a smooth surface. Another angle is the so-called apparent contact angle  $\beta$ , which is macroscopically observed in the drop placed on the textile surface. The difference between angles is related to the tilt of the monofilament surface in the contact place of liquid with the monofilament against the horizontal plane. Angle  $\gamma$  describes the slope of weft in the contact place of the surface drop with the surface of the monofilament.

The surface of the wetting liquid was approximated in the area of the contact point by using a line, because the curvature of the drop can be here neglected - the curvature of the monofilament surface  $S_1$  and  $S_2$  is significantly higher than that of the drop surface  $S_3$ .

The course of the monofilament surface in the fabric marked  $S_I$  was defined on the basis of generally accepted ideas about the geometry of the fabric as a sine curve:

$$S_1 = 3r + r \cdot \cos\left(\frac{\pi \cdot x}{X}\right) \tag{3}$$

where:

- r is the radius of the monofilament yarn,
- x the coordinate axis x and
- X is the distance between two perpendicular monofilaments in the system.

The surface of the perpendicular monofilament  $S_2$  is projected as a circle. From the equation for a circle and geometry of the system we can deduce the course of surface  $S_2$  with the equation :

$$S_2 = 3r + \sqrt{r^2 - (x - X)^2}$$
(4)

Then simple equations which describe the model were derived to determine the relationship between the real contact angle  $\alpha$  and apparent contact angle  $\beta$ :

$$S'_{1} = -\frac{\pi \cdot \mathbf{r}}{X} \cdot \sin\left(\frac{\pi \cdot \mathbf{x}}{X}\right)$$
(5)  
$$S'_{2} = \frac{\mathbf{x} - \mathbf{X}}{3\mathbf{r} - S_{2}}$$
(6)

Furthermore a general equation of the tangent to curve  $S_2$  at point  $x_T$  corre-



**Figure 2.** Behaviour of a drop on the monofilament surface – situation of advancing contact angle.



*Figure 3.* Behavior of the drop on the monofilament surface – situation of receding contact angle.

sponding to the limit state of liquid in contact with the fabric was determined and is presented as Equation (7):

$$y = x \cdot \frac{x_{T} - X}{3r - S_{2T}} + \frac{-x_{T} \cdot X + X^{2} - 3r \cdot S_{2T} + 8r^{2}}{3r - S_{2T}}$$
(7)

where index T relates to corresponding contact angles  $\alpha$  and  $\beta$  to the contact point of surfaces  $S_2$  and  $S_3$ .

The point of intersection  $x^*$  of  $S_1$  and tangent to curve  $S_2$ :

$$x^* = \frac{X}{\pi} \cdot \arccos\left(\frac{ax+b-3r}{r}\right) \qquad (8)$$

Based on previous equations, the apparent contact angle  $\beta$  and angle  $\gamma$  were determined:

$$\beta \Rightarrow \beta = \operatorname{arctg}\left(\frac{\mathbf{x}_{\mathrm{T}} - \mathbf{X}}{3\mathbf{r} - \mathbf{S}_{2\mathrm{T}}}\right)$$
 (9)

$$\gamma \Longrightarrow \gamma = \operatorname{arctg}(\mathbf{S}_1' \cdot \mathbf{x}^*) \tag{10}$$



**Figure 4.** Dependence of apparent contact angle  $\beta$  on real contact angle  $\alpha$  – comparison of theoretical model proposed (curves) and experimental results (points).

#### Experimental part

In this work we determined the real contact angle  $\alpha$  and apparent contact angle  $\beta$  according to the abovementioned equations. Furthermore we compared the results of contact angles determined by the theoretical model and experimental results. For the experimental study we used textile made from polyethylene terephtalate mono-filaments (Silk&Progress) with the following parameters: No. ends / No. picks is 43/43 in 1/cm, and the fibre diameter for warp/weft is 80/80 in  $\mu$ m. The structure corresponds to the description in the model.

Before the experiment, the surface of the material was washed in distilled water. Next followed extraction with Dichloromethane G. R. stabilised (Lach - Ner). For the measurement, distilled water with a surface tension of  $72.5 \pm 0.2 \text{ mN} \cdot \text{m}^{-1}$ at 20 °C was used. To measure the contact angles the sessile drop method was applied. A known volume (5 µl) of test liquid was either added or removed using a microsyringe. In this method the microsyringe needle was placed close to the surface and the drop was slowly applied. Advancing and receding angles on the same drop were measured after each addition or removal of water volume by the device See Standard System (Advex Instruments Ltd., Czech Republic). This system is a portable computer-based instrument designed for contact angle measurement and surface energy determination. It contains a colour camera with 1.3 MPix resolution movable in a vertical direction and 2D horizontally movable table for samples. The sessile drop, sitting on the surface of sample, was viewed via a camera on the computer display.

### Results and discussion

Based on concrete parameters of simple plain weave fabric and the above-mentioned equations, a theoretical model of water drop behaviour was determined. The model was solved for two situations: advancing the contact angle and receding contact angle. From values of the real contact angle  $\alpha$  and apparent contact angle  $\beta$ , their mutual relationship was determined, which we can observe in *Figure 4*.

Simultaneously we measured the wetting on the textile fabric, and for comparison on a smooth plate as well. The advancing and receding contact angles were determined by measurement. The contact angles were measured with an accuracy of  $\pm 2^{\circ}$  and the average values of contact angles were determined from 10 measurements. From the experimental data, it was established that contact angle values are higher for textile in comparison with a smooth plate. Several measured values were plotted on a graph and compared with those of the numerical solution (see *Figure 4*).

In *Figure 4* we can see the values of contact angles for the untreated sample and for the treated sample. In the case of the treated sample the material is hydrophobised by two types of commonly available hydrophobic agents: Waterstop and Aquastop according to the producer's recommendations. From the results, it can be seen that the data measured are close to those of the theoretical model. The theoretical curve of the advancing contact angle and receding contact angle curve represent the limits to which the data approaches but do not exceed.

From the theoretical model, it is possible with concrete textile fabric to estimate the approximate value of the apparent contact angle  $\beta$  from the curves if we know the angle  $\alpha$ , which corresponds to that measured on smooth surfaces.

#### Conclusion

It was learned long ago that wetting is affected not only by material properties but also by the surface geometry. The situation is especially complicated in textiles with respect to yarn twist, yarn hairiness and type of weave. In our case we used a basic fabric made from polyethyleneterephtalate monofilaments, on which was estimated the advancing and receding contact angles. Along with this process, a theoretical model is proposed which predicts the advancing and receding contact angles of drops on woven structures. In our work we found that the limits of wetting behaviour (advancing and receding contact angles) can be described by two curves: The curve for the advancing contact angles, and that for the receding contact angles. The real measured contact angles of a woven structure must be located between these two theoretical functions. This model represents the first useful connection between the geometry of a woven structure surface and the real values of advancing and receding contact angles. 

#### References

- Zisman WA. Contact angle, wettability and adhesion. *Advances in Chemistry Series* 1964; 43: 1-51.
- Li D, Neumann AW. Advances in Colloid and Interface Science 1992; 39: 299-345.
- Fowkes FM. Industrial & Engineering Chemistry 1964; 56, 12: 40-52.
- Kwok DY, Neumann AW. Advances in Colloid and Interface Science 1999; 81, 3: 167-249.
- Spelt JK, Li D. The equation of state approach to interfacial tensions. In: Neumann AW, Spelt JK (eds) *Applied Surface Thermodynamics*. Marcel Dekker Inc., New York 1996, pp. 239-292.

- van Oss CJ, Chaudhury MK, Good RJ. Chemical Reviews 1988; 88, 6: 927-941.
- 7. Young T. Philosophical Transactions of the Royal Society 1805; 95: 65-87.
- Lam CNC, Wu R, Li D, Hair ML, Neumann AW. Advances in Colloid and Interface Science 2002; 96, 1-3: 169-191.
- 9. Bartell FE, Shepard JW. Journal of Physical Chemistry 1953; 57, 2: 211-215.
- 10. Johnson Jr. RE, Dettre RH. Advances in Chemistry Series 1964; 43: 112-135.
- Eick JD, Good RJ, Neumann AW. Journal of Colloid and Interface Science 1975; 53, 2: 235-238.
- 12. Oliver JF, Huh C, Mason SG. *Colloids* and Surfaces 1980; 1, 1: 79-104.
- Johnson Jr RE, Dettre RH. Journal of Physical Chemistry 1964; 68, 7: 1744-1750.
- Neumann AW, Good RJ. Journal of Colloid and Interface Science 1972; 38, 2: 341-358.
- 15. Schwartz LW, Garoff S. *Langmuir* 1985; 1, 2: 219-230.
- 16. Derjaguin BV. *CR Acad. Sci.*, USSR 1946; 51: 361.
- Johnson Jr. RE, Dettre RH. In: Surface and Colloid Science (E. Matijevic, Ed.), Wiley–Interscience, New York, 1969, pp. 85-153.
- Brandon S. Marmur A. Journal of Colloid and Interface Science 1996; 183, 2: 351-355.
- Timmons CO, Zisman WA. Journal of Colloid and Interface Science 1966; 22, 2: 165-171.
- 20. Decker EL, Garoff S. *Langmuir* 1996; 12, 8: 2100-2110.
- 21. Decker EL, Garoff S. *Langmuir*, 1997; 13, 23: 6321-6332.
- 22. Chen W, McCarthy TJ. *Macromolecules* 1997; 30, 1: 78-86.
- 23. Youngblood JP, McCarthy TJ. *Macromolecules* 1999; 32, 20: 6800-6806.
- Lam CNC, Ko RHY, Yu LMY, Ng A, Li D, Hair ML. Neumann AW. *Journal of Colloid and Interface Science* 2001; 243, 1: 208-218.
- 25. Marmur A. *Langmuir* 1996; 12, 23: 5704-5708.
- 26. Wolansky G, Marmur A. *Langmuir* 1998; 14, 18: 5292-5297.
- Wolansky G. Marmur A. Colloids and Surfaces A: Physicochemical and Engineering Aspects 1999; 156, 1-3: 381– 388.
- Gocławski J, Urbaniak-Domagała W. Fibres & Textiles in Eastern Europe 2008; 16, 2(67): 84-88.
- 29. Petrulyte S, Baltakyte R. *Fibres & Textiles in Eastern Europe* 2008; 16, 4 (69): 62-66.
- Dembický J, Wiener J. Fibres & Textiles in Eastern Europe 2010; 18, 5 (82): 51-54.

Received 20.01.2012 Reviewed 30.05.2012





# XIPS 2013

## 9<sup>th</sup> International Conference on X-Ray Investigation of Polymer Structure

3-6 DECEMBER 2013, Zakopane, POLAND

XIPS 2013 is organised by the University of Bielsko-Biała and Catholic University of Leuven in collaboration with the Committee on Materials Science of the Polish Academy of Sciences

#### **Deadlines:**

- registration and payment: 15.09.2013
- abstracts: 15.10.2013

#### CONFERENCE TOPICS

The triennial XIPS conference provides a forum for discussions related to the present state of methods and achievements in structural investigations of polymers.

The conference will feature a wide range of topics, including:

- X-ray and neutron scattering techniques,
- X-ray imaging, IR and NMR spectroscopy in studies of polymers and their composites, colloids, porous media, membranes, surfactants and biomaterials
- Development of methods and techniques in X-ray studies of soft matter
- Software and databases for soft matter structure investigations
- Analysis of X-ray and neutron scattering data and modeling of material structure
- Morphology and thermal behaviour of polymer materials

#### Chairman of the INTERNATIONAL ADVISORY BOARD Harry Reynaers Catholic University of Leuven, Belgium

#### Contact

University of Bielsko-Biała Institute of Textile Engineering and Polymer Materials Willowa 2, 43-309 Bielsko-Biala, Poland tel. (+48 33) 82 79 151 fax.(+48 33) 82 79 100 e-mail: mbasiura@ath.bielsko.pl http://www.xips.ath.bielsko.pl/