

DETERMINATION OF SURFACE FREE ENERGY OF POLYAMIDE, POLYPROPYLENE AND POLYETHYLENETEREPHTHALATE SURFACES FROM CONTACT ANGLE HYSTERESIS

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Abstract:

Contact angle measurement is a method of surface characterisation of solid materials. The basis of this measurement is to determine the surface energy of solids and thus obtain information on the behaviour of the surface: if it, for example, applies a thin layer on the surface of another material. The surface energy can be determined using contact angle hysteresis, which was used in this work.

Key words:

Contact angle hysteresis, surface free energy, textiles and smooth plates.

Introduction

There is ample experimental evidence that when a sessile drop is first placed on a solid surface, the apparent contact angle is larger than the equilibrium contact angle, sometimes by several degrees [1]. In a similar way, if liquid is removed from the droplet, the apparent contact angle is smaller than the equilibrium contact angle [2]. Thus, multiple values of contact angles can be measured, even on surfaces that are smooth and homogeneous [3].

In practical systems, even under static conditions, at least two different contact angles can be measured on the same solid surface and for the same liquid, which are termed advancing and receding contact angles. The difference between them is called contact angle hysteresis [4]. Up to now, the appearance of hysteresis was recognised mostly in terms of surface roughness and/or its heterogeneity [5-10]. Erbil et al. [11] listed five reasons for the appearance of contact angle hysteresis, namely surface roughness, microscopic chemical heterogeneity, drop size effect, molecular reorientation, and the penetration of liquid molecules into the solid surface. It appeared that, except for evidently rough and heterogeneous surfaces causing hysteresis, the advancing and receding contact angles differ even on molecularly smooth surfaces [12].

Thus, having measured the advancing and receding contact angles for a probe liquid, the total surface free energy of the solid can be evaluated, which is an apparent value resulting from the interactions present on the liquid/solid interface.

The contact angle is an important parameter in surface science. It is common practice that advancing contact angles are used in Young's equation to calculate solid surface free energy components [13-17]:

$$\gamma_S = \gamma_{SL} + \gamma_L \cdot \cos \theta_A \quad (1)$$

where γ_S is the solid surface free energy, γ_{SL} is the solid liquid interfacial free energy, γ_L is the liquid surface tension, and θ_A is the advancing contact angle. It can be assumed that, when retreating from the line of contact of the droplet for which the

advancing contact angle has just been measured, a film is left behind. If so, because of the presence of the film, the solid surface free energy is changed, but Young's equation in a modified form can still be utilised to describe this system [16]:

$$\gamma_{SF} = \gamma_{SL} + \gamma_L \cdot \cos \theta_R \quad (2)$$

where γ_{SF} is the film-covered solid surface free energy and θ_R is the receding contact angle. Then, the free energy of the film-covered surface can also be expressed by the following:

$$\gamma_{SF} = \gamma_S + \pi \quad (3)$$

where π is the film pressure.

Because the liquid does not spread spontaneously over the solid surface, the film pressure must be positive, i.e. the film increases the apparent free energy of the solid surface in the vicinity of the retreated droplet. If a liquid does not form any definite contact angle, i.e. its surface tension is less than the solid surface free energy, then the film pressure is negative, and in Eq. (3) it will have a negative sign. Next, by combining Eqs. (1) through (3), an equation describing the film pressure can be obtained:

$$\pi = \gamma_L (\cos \theta_R - \cos \theta_A) \quad (4)$$

If, for a liquid droplet settled on a solid surface, the advancing and receding contact angles were measured, and keeping in mind that the interfacial solid liquid free energy can be expressed by the following [15, 18-20]:

$$\gamma_{SL} = \gamma_S + \gamma_L - W_a \quad (5)$$

where W_a is the work of liquid adhesion, one can calculate from Eqs. (3) and (4) the work of adhesion for both advancing (A) and receding (R) modes, respectively:

$$W_a^A = \gamma_L (1 + \cos \theta_A) \quad (6)$$

$$W_a^R = \gamma_L (1 + \cos \theta_R) \quad (7)$$

Next,

$$W_a^R - W_a^A = \gamma_L(1 + \cos\theta_R) - \gamma_L(1 + \cos\theta_A) = \gamma_L(\cos\theta_R - \cos\theta_A) \quad (8)$$

and hence the film pressure can also be expressed via the work of adhesion,

$$\pi = W_a^R - W_a^A \quad (9)$$

which is the difference between the liquid work of adhesion to the film-covered surface and the work of adhesion to the bare surface of this solid.

The total solid surface free energy can be described by these two contact angles only.

$$\gamma_s = \pi \frac{(1 + \cos\theta_A)^2}{(1 + \cos\theta_R)^2 - (1 + \cos\theta_A)^2} \quad (10)$$

or, using Eq. (4), it results in the following:

$$\gamma_s = \gamma_L(\cos\theta_R - \cos\theta_A) \frac{(1 + \cos\theta_A)^2}{(1 + \cos\theta_R)^2 - (1 + \cos\theta_A)^2} \quad (11)$$

In real systems, where a solid surface practically always possesses some imperfections (microheterogeneity) and roughness, some amount of the liquid will be left behind the drop, which forms the film. If this model works, the total surface free energy of a solid can be evaluated from three measurable parameters, i.e. the probe liquid surface tension and its advancing and receding contact angles measured on the solid surface [21-23].

Experimental

In this work, the advancing and receding contact angles were measured, and their hysteresis was determined. Smooth plates and textiles manufactured from polyamide 6.6, polypropylene and polyethyleneterephthalate were used to test wetting. From a theoretical point of view, the structure of a textile is characterised by considerable surface roughness and the periodic repetition of roughness. The 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 (Silk&Progress). A description of the textile materials follows in Table 1.

Table 1. Description of the textile materials.

Material	Type of fabric	No. ends /No. picks [1/cm]	Fibre diameter warp/weft [µm]
polyamide 6.6	woven	145/130	44/48
polyester	woven	62/62	55/80
polypropylene	knitted	-	103

The surface of the materials was first cleaned with distilled water and then extracted using dichloromethane G. R. stabilised (Lach - Ner). For measuring the contact angle, the sessile drop method was used. The contact angles were evaluated by Lucia G software (Laboratory Imaging, Czech Republic). As the test liquid, distilled water with a surface tension $\gamma_L = 72.75 \text{ mN.m}^{-1}$ at 20°C was used. The advancing contact

angle measurement began with a volume of 5 µl. Further drops were gradually added to the drop placed on the surface of the material up to a volume of 50 µl. The volume of each added drop was 5 µl. Similarly, the receding contact angles were measured from 50 µl to 5 µl after the removal of a specific volume of water (5 µl).

Results and discussion

The values of the contact angles that were measured for the specific drop volume for advancing θ_A and receding θ_R contact angles were determined. The values for the work of adhesion W_a^A and W_a^R were obtained according to Eq. 6 and Eq. 7. From to Eq. 9, the film pressure π was determined. Finally, using Eq. 10, we determined the final values of the total solid surface free energies γ_s , and from Eq. 5 the values of solid liquid interfacial free energies γ_{SL} were determined. All the measured and calculated values for all materials are listed in Tables 2-4. The results of total solid surface free energies γ_s and the solid liquid interfacial free energies γ_{SL} are shown in Figures 1-3.

From the results shown in Figures 1-3, it can be seen that there was a significant difference between the energies. If the surface energy of the solid is greater than the interface energy of the solid-liquid, the liquid on the surface of the solid will be spread in a continuous layer. Thus, the material is wetted. This was valid for smooth plates of all the materials used. Similar results were also recorded with the polyamide textile (Fig. 1). It can be seen that the interface energy of the solid-liquid increased for the textile, but in both cases (smooth plate and textile), the material was well-wetted.

Different results are obtained when the surface energy of the solid is less than that of the interface energy of the solid-liquid.

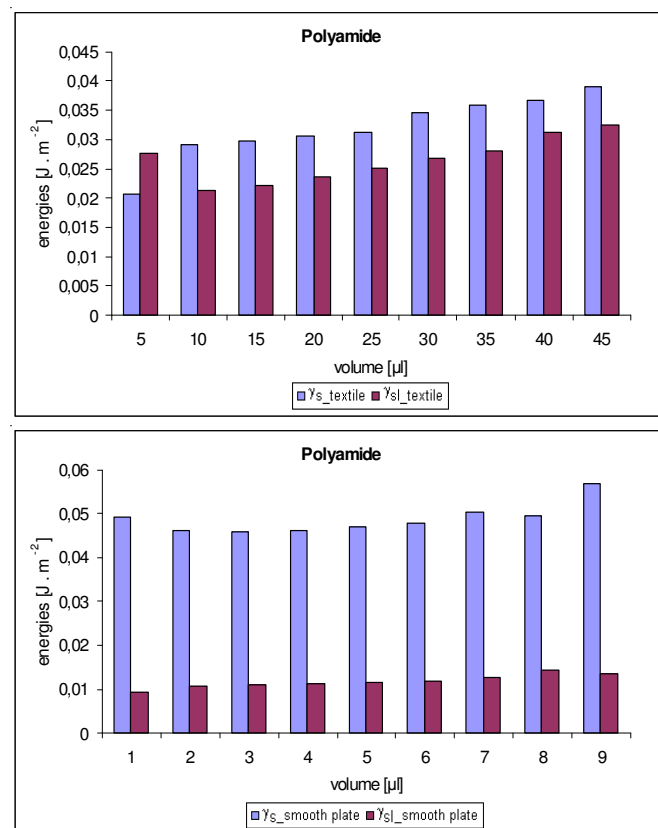


Figure 1. Energies for polyamide.

Table 2. Results for polyamide 6.6.

V [μl]	θ [°]				W _a [J.m ⁻²]				π [J.m ⁻²]	
	θ _A		θ _R		W _a ^A		W _a ^R		textile	smooth plate
	textile	smooth plate	textile	smooth plate	textile	smooth plate	textile	smooth plate		
5	95.5	56.7	12.8	0	0.0657	0.1127	0.1437	0.1455	0.0780	0.0328
10	83.8	60.8	16.0	0	0.0806	0.1082	0.1427	0.1455	0.0621	0.0373
15	84.0	61.3	28.5	7.3	0.0804	0.1077	0.1367	0.1449	0.0563	0.0372
20	84.5	61.2	39.6	11.1	0.0798	0.1078	0.1288	0.1441	0.0491	0.0363
25	85.2	61.1	49.8	21.7	0.0788	0.1080	0.1197	0.1403	0.0409	0.0324
30	83.8	60.5	61.8	26.5	0.0806	0.1086	0.1071	0.1378	0.0265	0.0292
35	83.8	58.6	67.8	35.8	0.0806	0.1107	0.1002	0.1318	0.0196	0.0211
40	85.7	61.1	77.8	41.2	0.0782	0.1080	0.0881	0.1275	0.0099	0.0195
45	84.8	53.7	82.9	48.1	0.0794	0.1158	0.0818	0.1214	0.0024	0.0055
50	87.3	57.1	87.3	57.1	0.0762	0.1123	0.0762	0.1123	0	0

Table 3. Results for polyethyleneterephthalate.

V [μl]	θ [°]				W _a [J.m ⁻²]				π [J.m ⁻²]	
	θ _A		θ _R		W _a ^A		W _a ^R		textile	smooth plate
	textile	smooth plate	textile	smooth plate	textile	smooth plate	textile	smooth plate		
5	105.2	80.0	0	0	0.0537	0.0854	0.1455	0.1455	0.0918	0.0601
10	89.8	68.7	16.9	17.8	0.0730	0.0992	0.1424	0.1420	0.0693	0.0428
15	90.2	76.2	38.7	31.9	0.0725	0.0902	0.1295	0.1345	0.0570	0.0444
20	93.7	74.3	55.0	36.7	0.0680	0.0924	0.1144	0.1311	0.0464	0.0387
25	95.3	75.8	66.3	48.4	0.0660	0.0906	0.1019	0.1210	0.0359	0.0304
30	96.2	73.5	75.9	54.5	0.0649	0.0934	0.0905	0.1150	0.0256	0.0216
35	99.6	76.6	84.8	55.6	0.0607	0.0897	0.0793	0.1139	0.0186	0.0242
40	100.8	74.9	92.7	62.3	0.0591	0.0918	0.0694	0.1066	0.0103	0.0148
45	102.9	74.1	96.7	69.6	0.0565	0.0926	0.0642	0.0981	0.0077	0.0055
50	102.7	76.0	102.7	76.0	0.0567	0.0903	0.0567	0.0903	0	0

Table 4. Results for polypropylene.

V [μl]	θ [°]				W _a [J.m ⁻²]				π [J.m ⁻²]	
	θ _A		θ _R		W _a ^A		W _a ^R		textile	smooth plate
	textile	smooth plate	textile	smooth plate	textile	smooth plate	textile	smooth plate		
5	126.1	95.3	32.5	16.7	0.0299	0.0660	0.1341	0.1424	0.1042	0.0764
10	117.5	77.4	45.0	41.1	0.0392	0.0889	0.1242	0.1275	0.0851	0.0389
15	115.2	75.9	75.9	36.5	0.0417	0.0905	0.0905	0.1312	0.0487	0.0408
20	116.2	79.5	86.9	39.3	0.0406	0.0860	0.0767	0.1290	0.0362	0.0430
25	126.8	80.7	94.7	45.1	0.0292	0.0844	0.0668	0.1241	0.0376	0.0397
30	127.0	75.9	107.2	49.2	0.0290	0.0904	0.0512	0.1203	0.0223	0.0299
35	121.4	77.1	114.2	53.2	0.0348	0.0891	0.0429	0.1163	0.0080	0.0273
40	120.1	78.5	119.9	60.4	0.0363	0.0872	0.0365	0.1087	0.0002	0.0215
45	121.8	76.3	121.7	69.5	0.0345	0.0900	0.0345	0.0982	0.00007	0.0082
50	122.6	78.9	122.6	78.9	0.0336	0.0868	0.0336	0.0868	0	0

Table 5. Ratio of the material and air components at the textile surface.

Material	Ratio of the components for textile surface		Smooth plate		Textile			
			Experimental values		Experimental values		Calculated values	
	material [%]	air [%]	γ _S [J.m ⁻²]	γ _{SL} [J.m ⁻²]	γ _S [J.m ⁻²]	γ _{SL} [J.m ⁻²]	γ _S [J.m ⁻²]	γ _{SL} [J.m ⁻²]
Polyamide 6.6	72	28	0.0488	0.0118	0.0320	0.0265	0.0351	0.0289
Polyethyleneterephthalate	70	30	0.0394	0.0204	0.0248	0.0338	0.0276	0.0361
Polypropylene	42	58	0.0358	0.0227	0.0128	0.0501	0.0150	0.0517

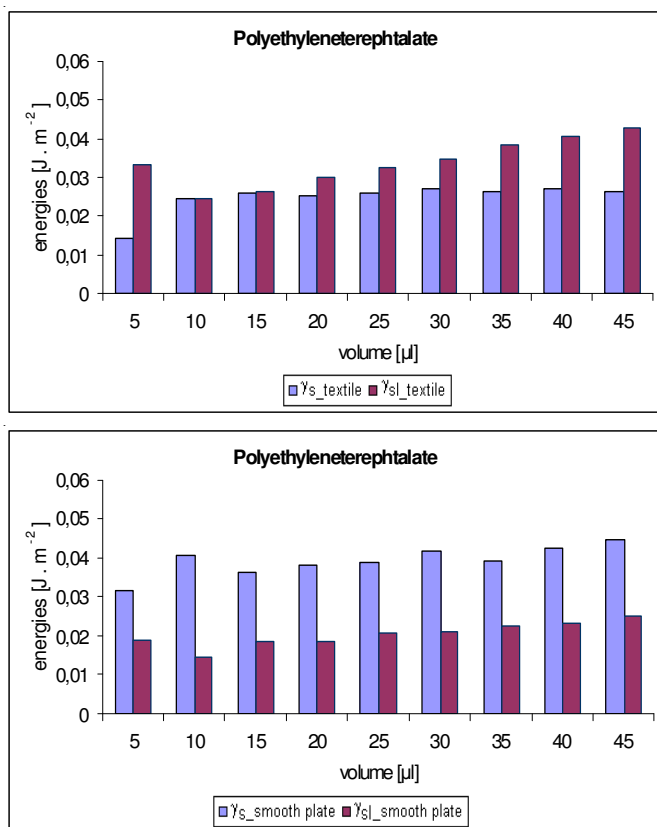


Figure 2. Energies for polyethyleneterephthalate.

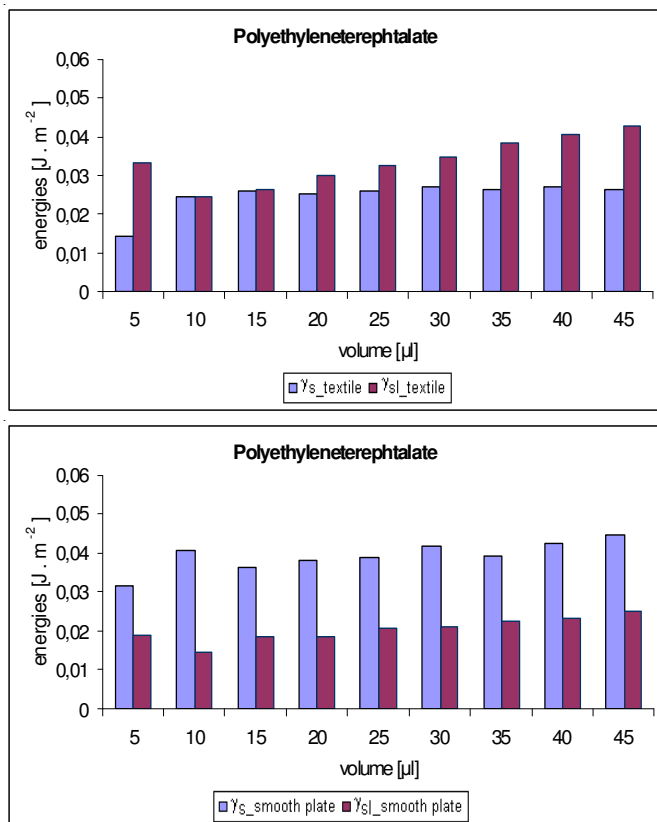


Figure 3. Energies for polypropylene.

In this case, a drop of liquid on the surface has a shape of equilibrium, which was shown in the other cases.

Polyethyleneterephthalate showed poorer wetting with increasing surface roughness. Similar results were found for

polypropylene, but the differences between the energies were very significant.

The influence of air enclosed in a liquid drop probably makes itself felt to some extent. In addition to surface roughness, the effect of air enclosed by a drop of liquid on a smooth material in contrast to a textile surface was also seen. For an ideal smooth surface, it is assumed that only the material is found under the drop of liquid. The situation is different with a textile. Here, it is considered that there is a greater percentage representation of the material and a smaller percentage representation of air. In our work, this assumption was taken into account for the textile and was applied by using the values of energies. For a dry material, it is valid that only the surface energy of the material γ_s asserts itself. For a wet material, the energy of the liquid γ_L and the interface energy γ_{SL} assert themselves. A representation of the percentage ratio of components was determined from the average energy values. To change the representation of the ratio of components, the minimum energy was found using the simple least squares method. For this energy value, the percentage ratio of all materials was deducted (listed in Table 5). A comparison of values was ascertained experimentally and calculated according to our assumption; see the following Equations (12, 13):

$$\gamma_{S(\text{calculated})} = \%_{\text{material}} \cdot \gamma_{S(\text{smooth_plate})} \tag{12}$$

$$\gamma_{SL(\text{calculated})} = \%_{\text{material}} \cdot \gamma_{SL(\text{smooth_plate})} + \%_{\text{air}} \cdot \gamma_L \tag{13}$$

It can be seen that the values differed very little, and it can be assumed that the approach was correct. The percent representation of material components increased under a drop of water in the following order: polypropylene, polyethyleneterephthalate, and polyamide. It follows that polypropylene provided a low level of attractive forces for polar liquids such as water and was thus hydrophobic. Therefore, air had a greater representation in the percentage of components. Polyamide had a high amount of attractive forces as a highly energetic material, was polar, and was the most water-wettable. Polyethyleneterephthalate was similar to polyamide in terms of wettability.

Conclusion

The most frequently used method for solid surface free energy determination is the measurement of the wetting contact angle. Measurements of advancing and receding contact angles were used to study the surface energy in this work. Hysteresis values were determined from these experimental results. Our study was conducted using polyamide 6.6, polyethyleneterephthalate, and polypropylene with smooth and rough surfaces to better understand the behaviour of wetting. For the smooth plates, the results showed that polyamide was a highly energetic material in comparison with the other materials. The textile results showed that the change in the behaviour of the polyamide textile was similar to the smooth plate made from the same material. For polypropylene and polyethyleneterephthalate, this situation was different.

These phenomena can be caused by the effect of the ratio of the material and air components at textile surfaces. This idea was verified in the current study.

References:

1. Chen, Y. L., Helm, C. A. and Israelachvili, J.N., *J. Phys. Chem.*, 1991, 95: 10736.

2. Chibowski, E., *Adv. Colloid Interface Sci.*, 2007, 133: 51.
3. Torrigiani, M., "Wetting in the Presence of Langmuir Films", MS Thesis, University of Alabama Huntsville, 2005.
4. Good, R.J., in: Good, R.J., Stromberg (Eds.), "Surfaces and Colloid Science", vol. 11, Plenum Press, New York, 1979.
5. Johnson, R.E., Dettre, R.H., *J. Phys. Chem.*, 1964, 68: 1744.
6. Neumann, A.W., Good, R.J., *Colloid Interface Sci.*, 1972, 38: 342.
7. Schwartz, L.W., Garoff, S., *Langmuir*, 1985, 1: 11.
8. Joanny, J.F., de Gennes, P.G., *J. Phys. Chem.*, 1984, 81: 552.
9. Li, D., Neumann, A.W., *Colloid Polymer Sci.*, 1992, 270: 498.
10. Marmur, A., *Adv. Colloid Interface Sci.*, 1994, 50: 121.
11. Erbil, H.Y., McHale, G., Rowan, S.M., Newton, M.I., *Langmuir*, 1999, 15: 7378.
12. Hunter, R.J., "Foundations of Colloid Science", Clarendon, Oxford, 1995.
13. Lam, C.N.C., Kim, N., Hui, D., Kwok, D.Y., Hair, M.L., Neumann, A.W., *Colloids Surf. A*, 2001, 189: 265.
14. Lam, C.N.C., Wu, R., Li, D., Hair, M.L., Neumann, A.W., *Adv. Colloid Interface Sci.*, 2002, 96: 169.
15. Adamson, A.W., Gast, A.P., "Physical Chemistry of Surfaces", sixth ed., Wiley, New York, 1997.
16. Good, R.J., Srivatsa, N.R., Islam, M., Huang, T.L., van Oss, C.J., *J. Adhesion Sci. Technol.*, 1990, 4: 607.
17. van Oss, C.J., Giese, R.F., Wu, W., *J. Dispersion Sci. Technol.*, 1998, 19: 1221.
18. van Oss, C.J., Good, R.J., Chaudhury, M.K., *Chromatogr.*, 1987, 391: 53.
19. van Oss, C.J., Good, R.J., *Macromol. Sci.-Chem. A*, 1989, 26: 1183.
20. van Oss, C.J., Good, R.J., in: Loeb G. (Ed.), "Modern Approaches to Wettability: Theory and Application", Plenum Press, New York, 1992.
21. Chibowski, E., in: Mittal, K.L. (Ed.), "Contact Angle, Wettability and Adhesion", VSP, Utrecht, 2002, 2.
22. Chibowski, E., Perea-Carpio, R., Ontiveros-Ortega, A., *J. Adhesion Sci. Technol.*, 2002, 16: 1283.
23. Chibowski, E., *Adv. Colloid Interface Sci.*, 2003, 103: 149-172.

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