

Different approaches for the calculation of the surface free energy of conventional lithographic plates

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Abstract

A sessile drop instrument was constructed in order to measure the surface energy of lithographic plates by a video analyzing image device. This measurement is based on the dimension and shape of a liquid drop lying on the solid, with a resolution of 512 x 512 pixel/line.

First of all, PE and PTFE surfaces were tested.

This instrument was used to measure the contact angle of various liquids on the image areas of a positive and a negative lithographic plate, both before and after exposure and development. The surface free energy of the solid surfaces was calculated according to Fowkes', Owens Wendt's, Zisman's, Ström's and Van Oss' approaches.

Introduction

Contact between liquids and solids are frequently encountered in a large variety of fields including coating, adhesion, textile and printing.

In the lithographic printing process, non-image areas are covered with water, whereas image areas receive the ink. It is then important to determine the surface energy of the solid in order to optimise what will

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happen during the process.

In this first study, we are dealing with the image area of the plate which is constituted by the photopolymer layer.

Different approaches to evaluate surface energy

- Fowkes

This method is based on the idea that the work of adhesion is the sum of all the contributions of the different molecular interactions.

Fowkes (1980) used the geometric mean in order to calculate the dispersive component and lumped all the non-dispersive interactions under the term I_{SL} .

The work of adhesion W_{SL} can thus be written as :

$$W_{SL} = \gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_s^d \gamma_L^d} + I_{SL} \quad (1)$$

For systems including only dispersive interactions, viz. with a totally dispersive liquid, it is possible to obtain the dispersion contribution of the surface energy of the solid, γ_s^d . After that, one can determine the I_{SL} term with each liquid.

This procedure never gives the total surface energy of a solid considering that it depends on the liquids used.

- Owens-Wendt

Owens and Wendt (1969) extended Fowkes' approach, assuming that the dispersive and the polar components of the surface energy can be calculated using geometric means. Thus :

$$W_{SL} = \gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_s^d \gamma_L^d} + 2\sqrt{\gamma_s^p \gamma_L^p} \quad (2)$$

$$\text{with :} \quad \gamma_s^d + \gamma_s^p = \gamma_s \quad (3)$$

$$\gamma_L(1 + \cos \theta) / 2\sqrt{\gamma_L^d} = \sqrt{\gamma_s^p \gamma_L^p} / \sqrt{\gamma_L^d} + \sqrt{\gamma_s^d} \quad (4)$$

A plot of $\gamma_L(1 + \cos \theta) / 2\sqrt{\gamma_L^d}$, vs. $\sqrt{\gamma_L^p} / \sqrt{\gamma_L^d}$ should give a straight line with slope $\sqrt{\gamma_s^p}$ and intercept $\sqrt{\gamma_s^d}$.

- Zisman (1950)

This approach calls upon the idea of a critical surface tension for wetting, γ_c , which corresponds to the maximum surface tension that a liquid must reach in order to spread spontaneously on a solid, $\theta = 0$. A

series of well known liquids of different surface tension are used to determine contact angles on the solid. The function $\cos \theta$ vs. γ_L should give a straight line which is extrapolated to $\cos \theta = 1$ to evaluate the γ_c of the solid.

It is important to note that this energy depends on the liquids used for the establishment of the curve $\cos \theta$ vs. γ_L .

- Van Oss

Van Oss (1987) separated the surface energy into Lifshitz-Van der Waals interactions, γ^{LW} , and acid-base (donor/acceptor, hydrogen...) interactions, γ^{ab} :

$$\gamma = \gamma^{LW} + \gamma^{ab} \quad (5)$$

Van Oss defined a geometric mean function for the acid-base contribution, introducing γ^+ and γ^- as the acceptor and the donor character of the surface:

$$\gamma = \gamma^{LW} + 2\sqrt{\gamma^+\gamma^-} \quad (6)$$

In these conditions the work of adhesion is defined as :

$$W_a = 2\sqrt{\gamma_s^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_s^+\gamma_L^-} + 2\sqrt{\gamma_s^-\gamma_L^+} \quad (7)$$

From contact angle values of three liquids, the solution of the three-unknown equation system gives γ^{LW} , γ^+ et γ^- .

- Ström

Ström (1993) calculated the dispersive component, γ_s^d , by Fowkes' method. But he argued that the polar component cannot be evaluated by the geometric mean. So, he introduced a factor, K, which represents the hydrophilic character of a surface.

This parameter is given by the ratio :

$$K = W_{water/S}^{nd} / W_{water}^{nd} = W_{water/S}^{nd} / 2\gamma_{water}^{nd} \quad (8)$$

with,

$W_{water/S}^{nd}$: non-dispersive part of the work of adhesion between water and the solid

W_{water}^{nd} : non-dispersive part of the cohesive work of water

It is therefore possible to calculate K from the contact angle value of water on the solid.

The experimental system

- The system

The experimental system is presented in figure 1. The plate was placed on the holding test plate which could be levelled by a three-screw device. Then a drop of liquid was slowly formed by activating the motor which pushed on the piston of the glass syringe. It was thus possible to have drops of variable volumes (between 1 and 10 μ l), with a small error. Once the volume adjusted, the drop was placed on the solid surface and illuminated from behind with diffused light.

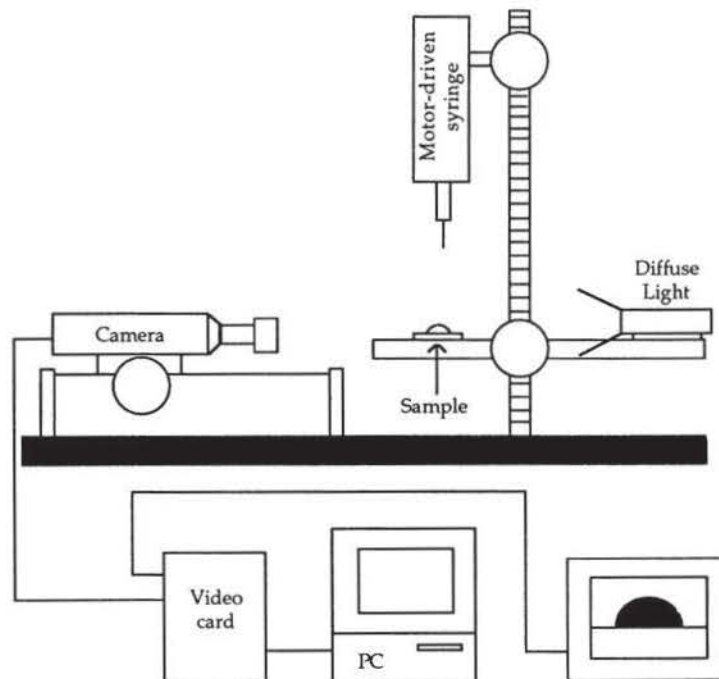
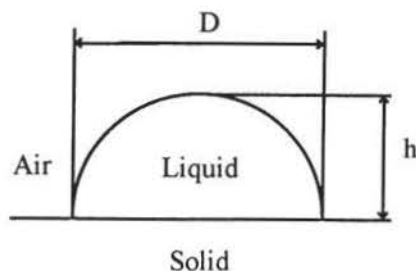


Figure 1 : Scheme of the experimental device

The image of the drop was seen on the monitor which was linked to the CCD camera. The signal from the video camera was fed to a digital acquisition card which converted it into a 256 grayscales image and a thresholding reduced it to a binary image by an appropriate pixel intensity magnitude choice.

We then determined the contact line between the liquid and the solid which allowed the program to evaluate the value of the contact angle by identifying three characteristic points of the drop.

The tangent to the contact angle is given by the formula :
 $\tan(\theta / 2) = 2h / D$,
for a spherical shape.



- Calibration of the system

A test card was placed in front of the video camera in the axis of the syringe in order to calibrate the system. Two digits on the screen allowed to calibrate the horizontal and two other digits the vertical axis.

It was also possible to check if the camera was in a horizontal position thanks to the test card.

Once the calibration done, the dimension of the screen pixel and the span of the screen were read on the monitor.

Calculation of the surface tension

A program was designed and developed on a computer in order to calculate the surface energy by the different approaches discussed above directly after having obtained contact angle values.

Values of the surface energy components for the test liquids

Table 1 gives the characteristics of test liquids used for the surface energy calculations.

Liquid	γ_L	γ_L^d	γ_L^p	γ^{LW}	γ^{ab}	γ^+	γ^-
water	72.8	21.8	51.0	21.8	51	25.5	25.5
methylene iodide	50.8	48.5	2.3	50.8	0.0	0.0	0.0
formamide	58.2	39.5	18.7				
α -bromonaphthalene	44.6	44.6	0				
glycerol	63.4	37.0	26.4	34.0	30.0	3.92	57.4

Table 1 : Surface tension components (mN/m) of the test liquids

Results and discussion

- Effect of the drop volume on the contact angle

The first step of the study was to examine the effect of the drop volume on the contact angle. We did different experiments on PTFE with water drops with volumes ranging from 0.6 μ l to 4.0 μ l. The results are given in table 2.

vol.(μ l)	θ ($^\circ$)	vol.(μ l)	θ ($^\circ$)
0.6	106.6	1.8	106.4
0.8	107.5	2.0	107.6
1.0	106.1	2.2	105.7
1.2	107.2	2.6	106.4
1.4	108.4	3.0	107.2
1.6	106.5	4.0	106.6

Tested surface : PTFE (Teflon)

Table 2 : Mean contact angle for different drop volumes

The results show (figure 2) that within this range of volumes, the drop size has no effect on the contact angle measurement, assuming that the error intrinsic to our setup is $\pm 1^\circ$.

Thereafter, polyethylene and PTFE of high purity were tested with distilled water drops of an average volume of 2 μ l.

$106^\circ \pm 1^\circ$ was found for PTFE and $102.2^\circ \pm 1^\circ$ for PE. Common values found in the literature are 108° and 102° . The method was therefore reliable and we decided to test other liquids.

The mean contact angle values obtained on PE and PTFE are given in table 3 and the surface energies in table 4.

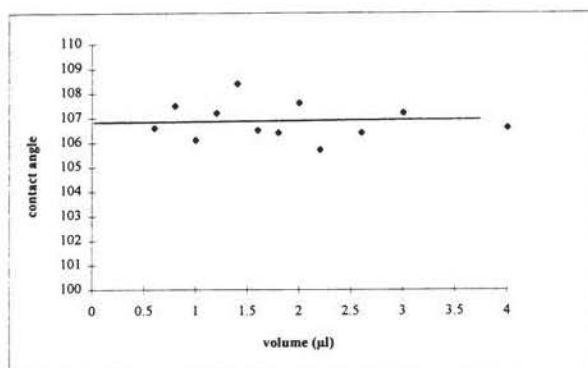


Figure 2 : Contact angle vs. volume of the drop

Liquid	PE		PTFE	
	θ	error	θ	error
- Water	102.2°	1°	106°	1.2°
- Formamide	80.5°	2.8°	95,3°	1.3°
- Methylene iodide	58.6°	1°	81,2°	0.8°
- Glycerol	80.1	2°	100,3	1.7°
- α -bromonaphthalene	30.1°	0.9°	71,3°	0.8°

Table 3 : Mean contact angle values for different liquids on PE and PTFE.

		PE	PTFE	
Owens-Wendt	γ_s^p	0.05	0.6	
	γ_s^d	33.9	16.5	
	γ_s	34.0	17.1	
Fowkes	water	I_{SL}	0.2	11.3
		W_{SL}	57.4	51.8
	met. iod.	I_{SL}	8.2	20.8
		W_{SL}	81.6	72.8
	glycerol	I_{SL}	-9.5	-2.8
		W_{SL}	77.3	58.6
Acid-base	γ^{L-W}	29.4	16.9	
	γ^-	0.02	1.9	
	γ^+	0.7	0.004	
	γ^{ab}	0.23	0.17	
	γ_s	29.6	17.1	
Zisman	γ_c	39.6	12.1	
Ström	K	0.002	0.1	

Table 4 : Surface energy (mN/m) for PE and PTFE.

The PE studied was a special high-purity sample with no additives kindly provided by BP France. It was stored under nitrogen in order to minimize any possible oxidation.

As expected, the PE surface was totally dispersive with negligible polar and acid/base components and very low non-dispersive interactions (as defined by Fowkes) with three liquids of different polarity (Table 4).

The PTFE was a commercial sample which could contain a small amount of additives which would explain the small degree of polarity observed for that surface. The total surface energies as calculated by Owens-Wendt's and Van Oss' approaches, (17 mN/m), are in good accordance with the results reported in the literature, whereas Zisman's critical surface tension, (12 mN/m), seems to be very low.

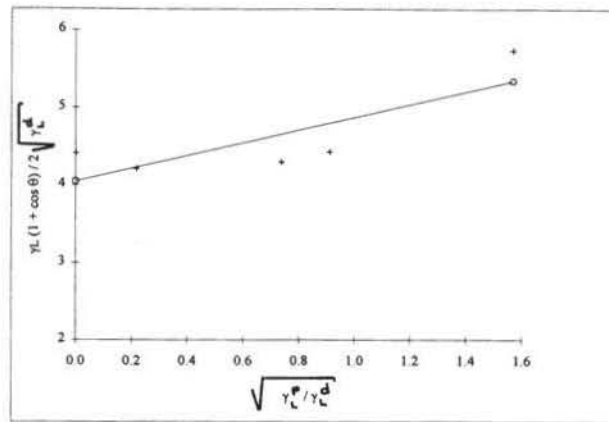


Figure 3 : Owens-Wendt's approach for PTFE

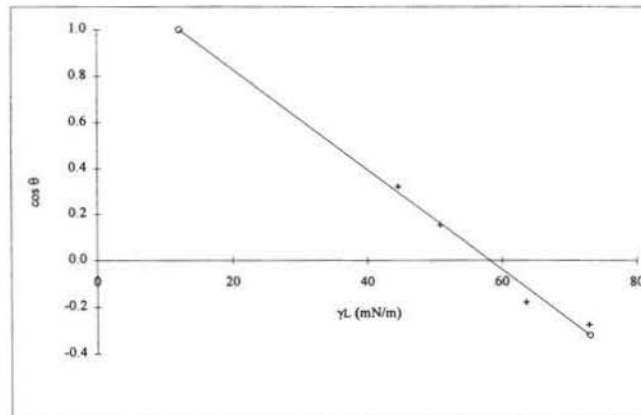


Figure 4 : Zisman's approach for PTFE

After this first round of experiments, the contact angles were measured on the image area of a negative and a positive plate, before and after exposure and development.

Table 5 gives the results arising from the different calculations.

		negative plate		positive plate		
		non exp.	dev.	non exp.	dev.	
Owens-Wendt	γ_s^p	3.0	4.4	1.1	1.0	
	γ_s^d	34.9	37.1	28.5	34.0	
	γ_s	37.8	41.4	29.7	35.0	
Fowkes	water	I_{SL}	26	30.5	16.4	15.8
		W_{SL}	82.1	89.5	68.1	71.2
	met. iod.	I_{SL}	3.2	0.7	1.1	2.5
		W_{SL}	88.2	90.4	79.7	86.7
	glycerol	I_{SL}	9.6	12.8	9.8	7.6
		W_{SL}	81.6	88.7	72.8	76.3
Acid-base	γ^{LW}	38.4	40.2	31.2	37.0	
	γ^-	5.9	7.5	2.1	2.1	
	γ^+	0.0002	0.07	0.01	0.001	
	γ^{ab}	0.06	1.4	0.34	0.8	
	γ_s	39.5	43.4	31.3	38.2	
Zisman	γ_c	38.9	41.6	32.8	38.7	
Ström	K	0.26	0.3	0.16	0.15	

Table 5 : Surface tension values (mN/m) for positive and negative plate

We can conclude to a rather good correlation between the methods used in the context of the determination of the total surface free energy of the image area. Furthermore, the results are in good agreement with those given in the literature by Festko (1988) and Fowkes (1990).

The maximum difference (4 mN/m) is observed between Owens-Wendt surface energy and Zisman critical surface tension for the positive plate after development.

In a general way, we noticed that development increases the surface free energy of the plate. This effect is more pronounced in the case of the positive plate, where an increase of about 6 mN/m occurred, whatever the calculation method used.

The negative plate had a more hydrophilic character than the positive one (image area). This tendency is illustrated by a higher polar contribution to the surface tension with the negative plate, viz. $\gamma_s^p = 4$ mN/m for the negative plate and $\gamma_s^p = 1$ mN/m for the positive one.

Moreover, the I_{SL} values (Fowkes) concerning the couple water/solid and the K values (Ström) are about the double for the negative plate than for the positive one.

Looking at the results obtained with the acid-base approach, it seems that both plates have a low basic character, which is a little more pronounced for the negative plate. No acid character was observed. Thus, the resulting γ^{ab} is about zero, indicating that the polar part of the surface free energy observed by Owens-Wendt's approach is not due to acid-base interactions but more likely to dipole-dipole interactions.

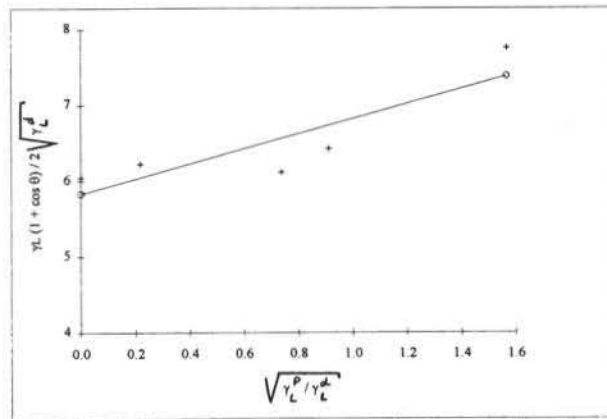


Figure 5 : Owens-Wendt's approach for the positive plate

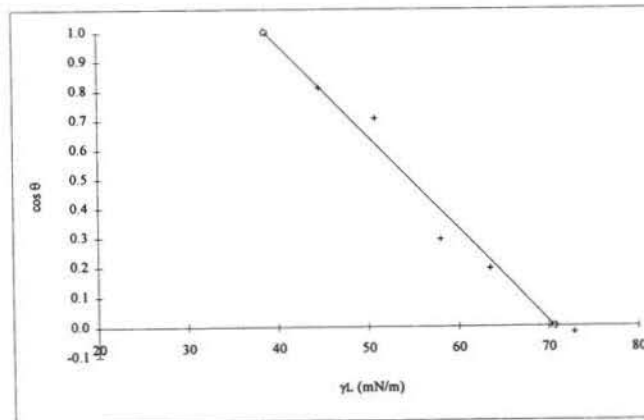


Figure 6 : Zisman's approach for the positive plate

Conclusion

The image analysis systems developed in the context of the determination of the surface free energy of lithographic plates proved to give reliable results.

The different approaches are in relatively good agreement for the image areas of the negative and positive plates studied here. The next step is to characterize the non-image area of the plates. This high energy surface requires the use of the so-called two liquids method based on contact angle measurements in a three-phase solid/liquid 1/liquid 2 system.

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