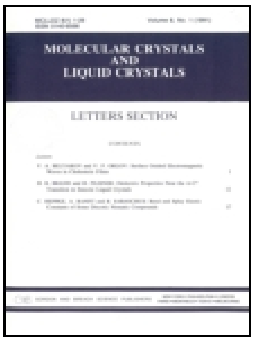

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Wilhelmy Plate Method of Polymer Film Surfaces for Printed Electronics

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To manufacture printed devices, the wetting and dewetting of inks on a plate is an important factor to achieve precise printing. The Wilelmy plate method is more precise than sessile drop method, but has never been applied to polymer films with different film sides as used in printable electronics. In this study, we applied the Wilhelmy plate method to unilaterally affixed polymer film and found a good agreement between the dynamic contact angles of affixed films and the corresponding original films. This provided the usability of Wilhelmy plate method for affixed film.

Keywords printed electronics; Wilhelmy plate method; dynamic contact angle; affixed film

Introduction

Roll to roll systems use polymer films as substrates for production of printable electronics. In this system, the polymer films are rolled in the first stage. To prevent the polymer film from sticking in the roll, front (printable) and back side of the polymer film surface are treated differently, and therefore, the two sides differ in their properties such as roughness and friction. Furthermore, front-side surface is modified to become suitable for printing. Polymer films for printed electronics do not have the same surfaces as pure polymer films and their front-side surfaces are also different from the back side surfaces.

The Wilhelmy plate method is superior to the Sessile drop method for the following reasons (1) high precision is achieved for contact angle estimation because of detection is carried out using a sensitive microbalance, which is free from human errors arising from visual determination; (2) high reproducibility is possible because of large scanning area (in order of cm square) of the substrates, and large amount of proving liquid, which reduces effect of evaporation and contamination to measurements; (3) reliable characterization of dynamic effects during the wetting and dewetting process is achieved through the accurate control of immersion and withdrawal speeds using a DC motor. However, the Wilhelmy plate method was originally designed for samples with the same surface. Therefore, it cannot directly be applied to polymer film surfaces for printed electronics because of the different properties of their front and back sides as shown in Fig. 1 [1,2]. Here, θ_f and

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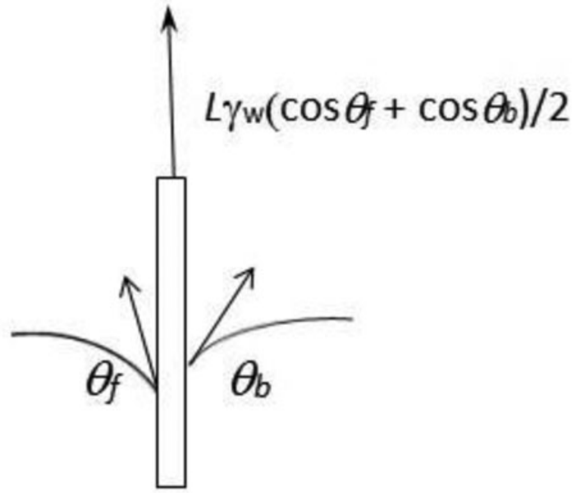

Figure 1. force acting on the film having asymmetric surface wettability.

θ_b are contact angles of front side and back side of sample film, L is perimeter of the film contacting with air/water interface, and γ_w is surface tension of water, respectively.

Experimental Setup

Dynamic contact angle measurements were carried out using the Kyowa Kaimen Kagaku Model DCA700 and water was used as the probing liquid. The measuring process comprised (1) at first, mechanically immersing mechanically 5 mm of the sample, and staying for 30 s, and withdrawing 5 mm of the sample (1st cycle), (2) next, immersing 7 mm and withdrawing 7 mm of the sample (2nd cycle) and, (3) finally immersing and withdrawing 10 mm of the sample (3rd cycle). The mechanical immersion and withdrawal speeds were 20 μm/s. Immersion depth difference between the cycles reveals an advanced contact angle difference between wetted and pre-wetted surfaces. The mechanical immersion depth is not exactly identical to the scanning position, i.e., the three-phase (air/water/film) contact line, because of the capillary rise of water [1,2]. Then, in this paper, we plotted the dynamic contact angles against the three-phase (air/water/film) contact line position (Z_{TPL}). 30 s stay in the 1st cycle was to clarify the effect of air/water interface on to polymer surface, which appears in the 2nd and 3rd cycles [1].

The sample used in the experiment, Q65HA (PEN: polyethylene naphthalate) and planarized PEN (Teijin Dupont Films Ltd.), SS120 (PC: polycarbonate) (TEIJIN Ltd.), and COSMOSHINE® (PET: polyethylene terephthalate) and XENOMAX ®(PI: polyimide)(Toyobo Co., Ltd.) were cut from the roll and sandwiched between protection films to prevent surface contamination. A fresh film surface was obtained by peeling off the protection film and exposing the original film. The procedure to fabricate a film that comprises front side surfaces only (affixed film (front)) is (1) peeling off protection film from the back side and affixing the back side to an adhesive thin film and (2) peeling protect film from the back side and affixing back side to the opposite side of the adhesive thin film. The used adhesive thin film is not soluble and does not swell in water. A film consisting only of back-side surfaces (affixed film (back)) was prepared in a similar manner except for peeling off protection film from the front side and affixing the front side to the adhesive thin film. Films were cut into pieces of 2 cm × 5 cm and residual protection films were peeled off before measuring the dynamic contact angle.

Results and Discussion

The dynamic contact angle patterns of planarized PEN of an original film, an affixed film (front), and an affixed film (back) are illustrated in Figures 2–4, respectively. Z_{TPL} intercepts of large constant contact angle indicates an advancing process, whereas Z_{TPL} intercepts of small are related to a receding process.

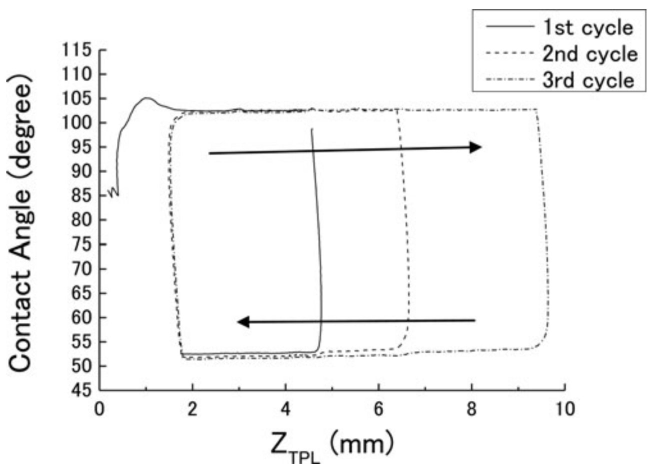

Figure 2. contact angles of θ^{adv} and θ^{rec} of an original film of planarized PEN film plotted against Z_{TPL}

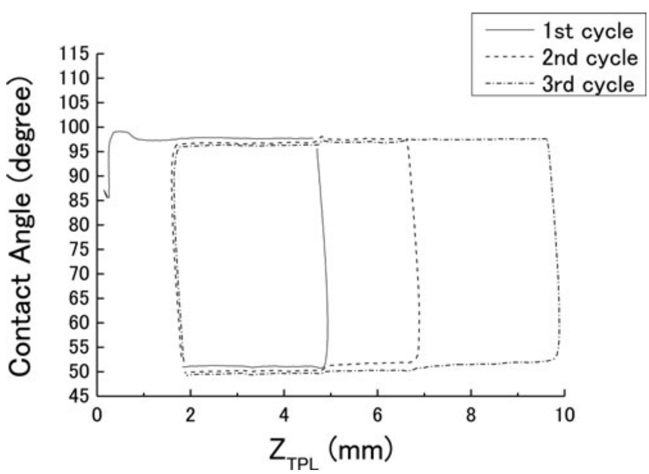

Figure 3. contact angles of θ^{adv} and θ^{rec} of an affixed film (front) of planarized PEN plotted against Z_{TPL}

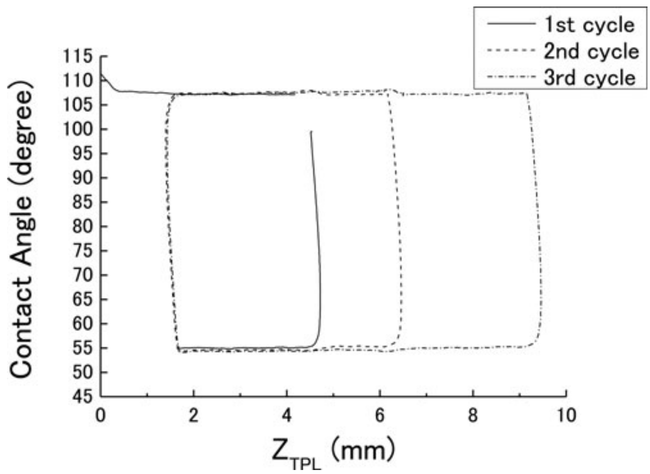

Figure 4. contact angles θ^{adv} and θ^{rec} of an affixed film (back) of Planarized PEN plotted against Z_{TPL}

Vertical lines at three-phase contact line positions Z_{TPL} less than 2 mm indicate an increase in contact angle with a constant value of Z_{TPL}. [1,2]: it starts when a receding process changes to an advancing one and terminates when the contact angle reaches the advancing contact angle. Similar lines are observed at Z_{TPL} value of more than 4 mm, corresponding to the reverse process: the contact angle changes from θ^{adv} to θ^{rec} at a constant value of $Z_{TPL.}$ Figures 3 and 4 differences in the dynamic contact angles; both advancing and receding contact angles are smaller in the affixed film (front) than in the affixed film (back).

The dynamic contact angle features of all films (original films, affixed film (front) θ_f and affixed film (back) θ_b) are summarized in Tables 1, 2, and 3, respectively.

Table 1. Dynamic contact angle of original film

Original film		1st cycle		2nd cycle		3rd cycle	
		$\theta^{adv*}/\circ$	$\theta^{rec}/\circ$	$\theta^{adv}/\circ$	$\theta^{rec}/\circ$	$\theta^{adv}/\circ$	$\theta^{rec}/\circ$
Q65HA (PEN)	pre-wetted	98	—	100	—	100	—
	wetted	—	54	97	55	98	55
Planarized PEN	pre-wetted	102	—	103	—	103	—
	wetted	—	52	102	53	102	53
SS120 (PC)	pre-wetted	97	—	99	—	100	—
	wetted	—	61	97	61	97	62
COSMOSHINE (PET)	pre-wetted	78	—	77	—	77	—
	wetted	—	36	82	36	82	36
XENOMAX (PI)	pre-wetted	83	—	83	—	83	—
	wetted	—	44	79	44	78	45

*θ^{adv} advancing contact angle, θ^{rec} receding contact angle

Table 2. Dynamic contact angle values of affixed film (front)

Affixed film (front)		1st cycle		2nd cycle		3rd cycle	
		$\theta^{adv*}/^\circ$	$\theta^{rec}/^\circ$	$\theta^{adv}/^\circ$	$\theta^{rec}/^\circ$	$\theta^{adv}/^\circ$	$\theta^{rec}/^\circ$
Q65HA (PEN)	pre-wetted	97	—	98	—	98	—
	wetted	—	63	98	64	98	64
Planarized PEN	pre-wetted	97	—	97	—	97	—
	wetted	—	50	97	51	97	51
SS120 (PC)	pre-wetted	98	—	98	—	99	—
	wetted	—	60	98	61	98	61
COSMOSHINE (PET)	pre-wetted	67	—	67	—	68	—
	wetted	—	47	73	47	73	48
XENOMAX (PI)	pre-wetted	84	—	83	—	84	—
	wetted	—	44	79	44	79	44

*θ^{adv} advancing contact angle, θ^{rec} receding contact angle

Table 3. Dynamic contact angles of affixed films (back)

Affixed film (back)		1st cycle		2nd cycle		3rd cycle	
		$\theta^{adv*}/^\circ$	$\theta^{rec}/^\circ$	$\theta^{adv}/^\circ$	$\theta^{rec}/^\circ$	$\theta^{adv}/^\circ$	$\theta^{rec}/^\circ$
Q65HA (PEN)	pre-wetted	96	—	97	—	98	—
	wetted	—	45	96	46	96	46
Planarized PEN	pre-wetted	107	—	108	—	107	—
	wetted	—	55	107	55	107	55
SS120 (PC)	pre-wetted	95	—	97	—	98	—
	wetted	—	59	95	59	95	59
COSMOSHINE (PET)	pre-wetted	92	—	92	—	92	—
	wetted	—	22	90	22	91	21
XENOMAX (PI)	pre-wetted	84	—	84	—	84	—
	wetted	—	42	79	43	78	43

*θ^{adv} advancing contact angle, θ^{rec} receding contact angle

The contact angle θ^{exp} of the original film can be predicted from the contact angle of the affixed films using the following equation.

$$\theta^{exp} = \cos^{-1}((\cos\theta_f + \cos\theta_b)/2) \tag{1}$$

The measured and expected contact angles of the original film are in good agreement with only small deviation of 3° or less. This proves that the affixed films are useful to measure dynamic contact angle by Wilhelmy method.

Here, we evaluate the dynamic contact angle data of the front side and the back side of the planarized PEN films (Figures 3 and 4) in more detail. Both -advancing and receding contact angles remain constant- indicating that the surfaces are homogeneous in sub-mm scale [1]. For the planarized PEN films, a small difference in the advanced contact angles θ^{adv} of the wetted and the pre-wetted surfaces is observed, which suggests only a small effect of water on the surfaces of the films. In the 2nd and 3rd cycles, there are no indicators that the air/water interface affects to the polymer surface [1]. Advancing and receding contact angles have similar values in both cycles, which demonstrates the stability of the film surface in water. On the other hand, the hysteresis ($\Delta\theta = \theta^{adv}$ - θ^{rec}) of the here measured dynamic contact angles is larger than that of most thiol-Au SAMs ($\Delta\theta < 10°$) [2]. – This means that planarized PEN films are not so stable and uniform as thiol-Au SAM having have well-ordered structure. – For printing electronics, this hysteresis and especially the receding contact angle, which is comparable to other films, should be taken into account.

Tables 2 and 3 indicate differences in the dynamic contact angles between affixed films (front) and affixed films (back) for all films, but their difference depends on the film variation. –Front and back surfaces do not only differ in roughness and friction but also in their wettability. – Differences in the advancing contact angles θ^{adv}, were observed between the wetted and the pre-wetted surface of some films. –Such a feature cannot observe by sessile drop method.– It is a sign of a water wetting effect on the film surface and can be vanished by washing the films with water before the measurements (Over the region of the films, all advancing contact angles indicate the same value in the wetted region). Because all used polymers do not sufficiently swell in water to produce a detectable error in the dynamic contact angle, this phenomenon results from a change in the surface properties. To better clarify this phenomenon, we will investigate it further and report these results in our future study.

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