

In situ enhancement of the surface free energy and polarity of polymers by electrocapillary rise wetting



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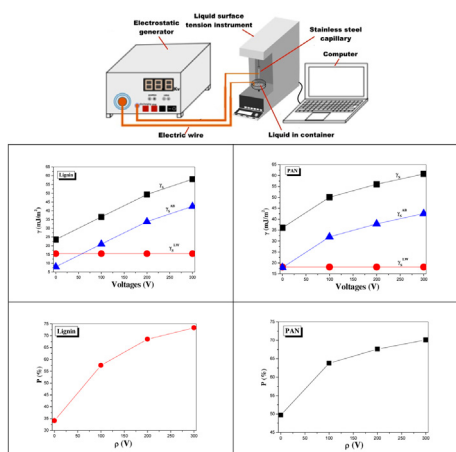
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HIGHLIGHTS

- The voltage increase can enhance the polar solvent adsorption for polymers.
- The voltage increase can enhance the surface free energy of polymers.
- The voltage increase can enhance the polarity of polymers.

GRAPHICAL ABSTRACT

Electrocapillary rise wetting induced *in situ* enhancement of the surface free energy and polarity of polymers.



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ABSTRACT

By applying the electrocapillary rise wetting, ECRW, with varied voltages and solvents to wet lignin and polyacrylonitrile, PAN, respectively, this work proven that this method can *in situ* enhance the surface free energy and polarity of polymers. Results showed that the voltage increase can *in situ* enhance the adsorption of only polar solvent by polymer to lead the reduction of related contact angle because of the adsorption of non-polar solvent by polymer ignoring the voltage variety. The diiodomethane was greatly adsorbed by both lignin and PAN due to the surface free energy of these polymers dominated by the non-polar Lifshitz-van der Waals interaction component. The voltage increase would enhance the Lewis acid-base interaction component of polymer to cause the enhancement of the surface free energy and polarity of polymers. This work showed that the polymer structure corresponding to the Lewis base may have different electric responses because the voltage increase has been found to cause the Lewis base component enhancement for ring structure-based polymer, e.g. lignin, and reduction for isotacticity structure-based polymer, e.g. PAN.

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1. Introduction

Since Lippmann found that an added electrostatic charge can significantly modify the capillary forces at an interface [1], the electrowetting was focused by many researchers and applied for various materials [2–8]. By applying the droplet-based electrowetting to wet some polymer surfaces using the water and decane probes, Janocha et al. [2] found that the contact angles, θ , between solvent and polymer would be varied with the voltage increase. In the same use of droplet-based electrowetting, Bratko et al. [9] found that the interfacial polar molecules would feature a strongly anisotropic response to the applied electric field to cause the dipole orientations parallel to the interface.

By employing an electrostatic generator to assist the common capillary rise wetting, CRW, we have recently developed an electrocapillary rise wetting, ECRW [10]. In the use of the ECRW and the probe polar/non-polar solvents, we found that the voltage increase can cause the polymer to show different adsorption behaviors, e.g. the adsorption of polar solvent in enhancement and of non-polar solvent in stable. The reason was furthermore found because the voltage increase would cause the surface tension of polar solvent to reduce [10–16].

The aim of this work is to apply the ECRW to study the wettability of polymers by deducing relative values directly from the dynamic adsorption curves. This is because that the ECRW can vary the polar liquid adsorption for polymer has been known [10], while the influence on the wettability of polymer yet unknown.

2. Experimental

2.1. Materials

Two commercial polymers were used, one is a natural polymer, alkali lignin, and another is a synthesized polymer, polyacrylonitrile, PAN. The former was purchased from Tokyo Chemical Ind. Co., Japan and the latter was obtained from Shanghai Jinshan Petrochemical Co. In this case, these two polymers were directly used as the same as previously without furthermore treatment [17–19].

Four solvents were employed as probes, e.g. the non-polar hexane and diiodomethane and the polar water and formamide. The physico-chemical parameters of these solvents cited from literature [8,9,11–18,20] were summarized in Table 1.

2.2. Electrocapillary rise wetting of polymers

The ECRW was performed as the same as previously described by employing an electrostatic generator to assist the common CRW by taking two electrodes respectively linking to the stainless steel tube and solvent [10].

For all runs, a stainless steel tube with inner diameter of 3 mm was used and charged of about 100 mg powder sample with a fixed height at about 4 cm to keep the packing density constant [10]. During the measurement, the stainless steel tube with charged polymer powder was hung on above a glass container with probe solvent, and then the container was gradually and slowly raised up to lead the solvent contacting the polymer at the bottom of stainless steel tube to allow the solvent spontaneously penetration into the powder polymer as the same as previously [10]. Once the solvent start wet the powder solid, the container movement was automatically stopped by computer controlled tensiometer and both the increased weight and time would be self-recorded by computer, respectively.

In this work, the applied voltage was varied at 0, 100, 200 and 300 V, respectively, and the presented data were averaged by three individual adsorption measurements at 25 °C.

3. Results and discussion

3.1. Effect of applied voltages on the adsorption of probe solvents by polymers

The adsorption of polar and non-polar solvents by two polymers in relation to varied electric voltages were presented in Fig. 1, where the adsorbed liquid amount by polymer at t time was defined as Q_t , g/g, as Eq. (1) described [10,25–28].

$$Q_t = W_{ad}/W_0 \quad (1)$$

where W_{ad} is the adsorbed liquid weight of solid at t time, g; and W_0 is the original weight of solid charged in stainless steel tube, g.

According to Fig. 1, both the polar and non-polar solvents can be adsorbed by these polymers, especially the diiodomethane, because it was greatly adsorbed as compared with other solvents in good agreement with our previously finding [10]. Additionally, Fig. 1 again proven that the voltage increase would enhance the adsorption of only polar solvents for polymers because the adsorption of non-polar solvent always in stable to ignore the voltage variety [10].

In order to quantitative analyze Fig. 1 appeared adsorption behavior for two polymers, we applied the Langmuir kinetics model [29,30] as Eq. (2) described to fit Fig. 1 presented adsorption curves as the same as previously [10,25–28]:

$$t/Q_t = 1/kQ_e^2 + t/Q_e \quad (2)$$

where k is the adsorption rate constant related to the second order Langmuir kinetics model, 1/s, and Q_e is the adsorbed amount by polymer at equilibrium state, g/g.

The obtained adsorption kinetics parameters of these two polymers in relation to all used solvents and voltages were summarized in Table 2. A comparison found that all solvents were greatly adsorbed by PAN and small by lignin suggesting the ring structure of lignin hardly absorption of liquid than that of the isotacticity structure of PAN. Since these two polymers both strongly in the LW component in their surface free energies [17–19] and both great adsorption of diiodomethane as compared with other solvents (Table 2), this implied that the LW interactions would be strongly occurred in liquid adsorption process [10]. In Table 2, the adsorption of water was found greatly for both PAN and lignin as compared with the formamide. The reason is due to these two polymers both strongly in the Lewis base component in their AB component [17–19]. Since the Q_e value (Table 2) is greater than Q_t value (Fig. 1), the reason should be addressed because the former is theoretically calculated from Eq. (2) while the latter is experimentally only representing one adsorption time.

Since the surface tension of polar liquid has been known to be reduced with the voltage increase [2,9–16], this induced influence on the wettability of polymer is interested and expected because the electric effect on surface free energy of polymers yet unknown.

3.2. Effect of applied voltages on the wettability of polymers

As has been known that the determination of the wetting result from the liquid adsorption process can apply the Washburn penetration equation as Eq. (3) described because this equation related to both the Q_t and contact angle, θ [29]:

(3) $Q_t^2/t = C\rho^2\gamma_L\cos\theta/\eta$ where C is a complex constant including the packing density, particle size and porosity; θ is the contact angle between liquid and solid.

Since the adsorption of hexane by all solids is a fully wetting to lead the $\cos\theta = 1$ [17,19,21–28], the C constant related two polymers charging in stainless steel tube could be directly determined from Eq. (3) and subsequently leading to determine the θ , for other

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