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# Water wettability/non-wettability of polymer materials by molecular orbital studies

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ABSTRACT

The water wettability and non-wettability onto various kinds of polymers, which have so far been macroscopically described by the water contact angle, were investigated using the molecular orbital theory. An atomistic model consisting of an $H_2O$ molecule and a selected polymer crystal surface was analyzed in the isolated and the physisorbed states. The degree of interaction between the water molecule and the polymer surface was evaluated by considering the change of Mulliken charge at the oxygen site in the water molecule, and also the work of adhesion during the physisorption process. Such energetic quantities for several polymers were compared with the macroscopic water wettability/non-wettability. We found fairly good agreement between these approaches for the highly non-wettability polymers.

## 1. Introduction

Wettability is the tendency of a liquid to spread on a solid substrate and is generally measured in terms of the contact angle, i.e., the angle between the substrate surface and the tangential line drawn at the triple point of the three phases (solid, liquid and gas) [1,2]. The water wettability/non-wettability of polymer materials are crucial to prospective applications of thin film materials, such as very thin optical displays [3,4]. The origin of the macroscopic water wetting/non-wetting phenomenon at polymer surfaces should ultimately be explainable in terms of the interaction between atoms of the water molecule and the surface of the polymer.

It is important to describe accurately the local electronic state dependent on the atomic configuration of the polymer [5]; hydrogen bonding in particular plays an important role in the dynamics and structure of water and water vapor [6,7]. Therefore, to take into account of the interaction between water and polymer materials, the local electronic state of the complete atomic system should be estimated by first-principle calculations such as density functional theory (DFT) calculations or by non-empirical molecular orbital (MO) methods. However, it is actually impossible to treat the van der Waals force, which affects the second and third-order structure of polymers, by DFT calculations. Moreover, non-empirical MO calculations have the serious limitation of employing periodic boundary conditions, which are necessary to model crystalline polymers. The other candidate computational scheme is semi-empirical molecular orbital (SEMO) calculations. In general, it is acknowledged that the accuracy of SEMO calculations for electrical states is not very high. However, SEMO calculations are accurate enough to express the mechanical behavior of a single polymer chain constructed with low atomic weight atoms such as hydrogen, carbon, nitrogen, oxygen and fluorine.

In the present study, we investigate water wettability and non-wettability of polymer materials from the atomic configurations of their molecular structures and the electric charge transferability using SEMO calculations. Also, the works of adhesion during the physisorption process of a water molecule for several polymers are compared with the macroscopic water wettability/non-wettability.

## 2. Calculation methodologies

### 2.1. Modelling of $H_2O$ and polymer crystal surfaces

In this study, the equilibrium structure of the atomic system and the interaction between the water molecule and various polymer surfaces are summarized by using a SEMO method based on a PM5 Hamiltonian; the latter is the latest revised version of PM3 [8,9] as coded in a general package MOPAC2006 [10,11]. Thirteen polymers are examined in this work: poly-(*p*-phenylene pyromellitimide) (PMDA-PDA; PI), polyethylene terephthalate (PET), poly(tetrafluoroethylene) (PTFE), polyethylene (PE), poly(ethylene-2,

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6-naphthalate) (PEN), polycarbonate (PC), polyether sulfone (PES), poly(*p*-phenylene terephthalamide) (AR), polypropylene (PP), poly (methyl methacrylate) (PMMA), poly(vinylidene chloride) (PVDC), polyetheretherketone (PEEK) and polyvinyl alcohol (PVA). Fig. 1 shows the equilibrium structures of the single molecular chain in unit cell of tested polymer materials. Since it is empirically thought that PVDC has two forms i.e., one with the chlorine atoms in the chain are in the uppermost position (i.e., closest to the polymer surface) and one in which the hydrogen atoms are uppermost, both atomistic models were employed in the present simulations. The former model is called PVDC1 and the latter PVDC2. To obtain the equilibrium atomic configuration of a single molecular chain of a given polymer, we determined the initial structure of one repeating unit cell using the Winmostar [12] program. Due to the specification of MOPAC2006, a periodic boundary condition along the molecular axis direction, for which the length must be taken to be more than 10 Å, was adopted to describe the repeating molecular chain. The initial structure was then relaxed using conjugate gradient (CG) algorithms [13]. The atomic positions were relaxed until the force at each atomic site reached a level of 10 meV/Å.

In order to investigate interactions between the water and the various polymer materials, atomistic models consisting of one water molecule and the in-plane periodic polymer crystal surface were constructed as follows. Two molecular chains were positioned in a unit cell perpendicular to the molecular axis ($x$ axis) direction. Periodic boundary conditions were set in the $y$ (perpendicular to the molecular chain) and $z$ (along the molecular chain) directions as shown in Fig. 1. The $H_2O$ molecule was relaxed and set 10 Å above the polymer crystal surface. The atomistic system containing $H_2O$ and polymer was then relaxed by CG algorithms to obtain the physisorbed states between the two species.

### 2.2. Change of Mulliken charge during physisorption process of $H_2O$ molecule on polymer surface

Mulliken population analyses were conducted for two of the physisorbed states and for the state of the isolated $H_2O$ molecule and polymer crystal surface. The change of Mulliken charge at each atom within the system between the isolated and the physisorbed states ($\Delta Q$ [29]) is given by

$$\Delta Q_i = Q_i^{\text{phy}} - Q_i^{\text{iso}} (1 \le i \le N), \tag{1}$$

where $N$ and $i$ are the total number of atoms in the system and the identification index of atom, respectively. The variables $Q_i^{\text{iso}}$ and $Q_i^{\text{phy}}$ indicate the Mulliken charge at each atom in the isolated and the physisorbed states, respectively. A positive value of $\Delta Q_i$ denotes a decrease in Mulliken charge. Since $\Delta Q_i$ indicates the change of effective charge at each atom during the physisorption process, one can determine the electrical change between the $H_2O$ molecule and polymer surface during the process using $\Delta Q_i$. In this study, particular attention is paid to the $\Delta Q_i$ of the oxygen atom (O-site) in an $H_2O$ molecule ($\Delta Q_O$) during the physisorption process to measure the degree of water wettability and non-wettability. Charge transfer should occur between the hydrogen and oxygen atoms in an $H_2O$ molecule under the physisorption process whenever $\Delta Q_O$ has any non-zero value, because the total electric charge of the $H_2O$ molecule in its isolated state is originally zero. When the absolute value of $\Delta Q_O$ is large, the change of electric charge at the O-site of the $H_2O$ molecule is large in back and forth of physisorption process.

### 2.3. Work of adhesion

From an energetic consideration of the wettability/non-wettability of polymer materials, works of adhesion have been proposed, defined in both macroscopic and microscopic schemes. In the former, Dupre defined the work of adhesion as the work per unit area to dissociate water from an inert solid surface, given by

$$W_a = \gamma_{SG} + \gamma_{LG} - \gamma_{SL}, \tag{2}$$

where $\gamma$ is the interfacial tension between two phases and the subscripts S, L, and G indicate solid, liquid, and gas phases, respectively. Inserting Young's equation, which is defined by

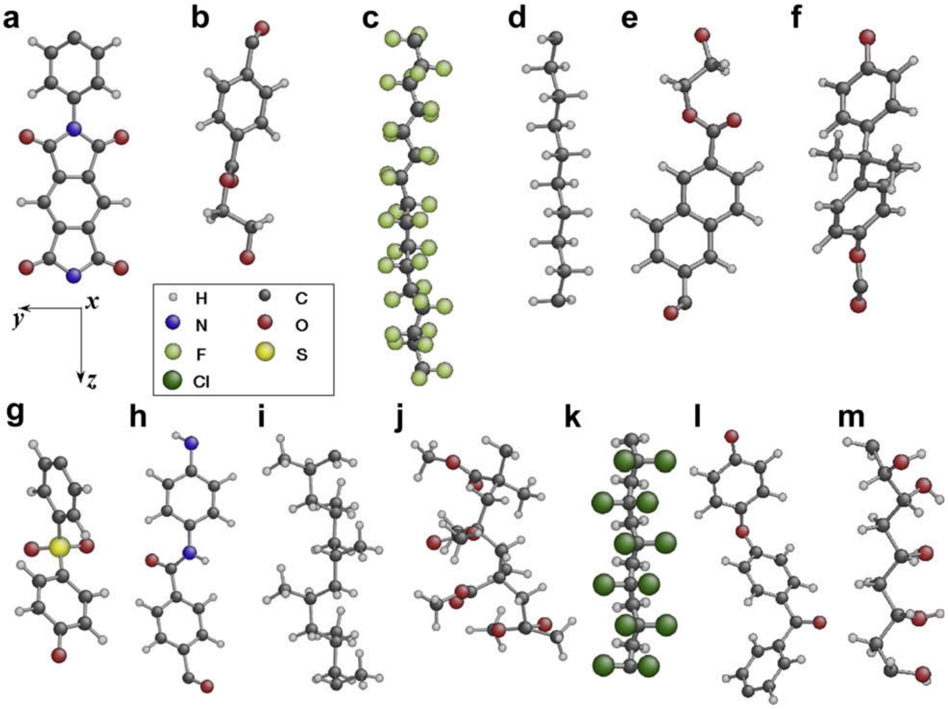

**Fig. 1.** The equilibrium structures of the single molecular chain in unit cell of tested polymer materials obtained from SEMO calculations. (a) PI(PMDA-PDA); (b) PET; (c) PTFE; (d) PE; (e) PEN; (f) PC; (g) PES; (h) AR; (i) PP; (j) PMMA; (k) PVDC; (l) PEEK; (m) PVA.

**Table 1**
Calculated (calcd) and experimental (exptl) lengths of one repeating unit of single molecular chain in the molecular axis direction and water contact angle (WCA) of tested polymer materials.

| Name of polymer | Calcd (Å) | Exptl (Å) | WCA (°) |
|---|---|---|---|
| PTFE | 19.79 | 19.50 [14] | 114 [20] |
| PET | 10.50 | 10.79 [14] | 70 [21] |
| PI | 12.40 | 12.2 [15] | 64 [22] |
| PE | 2.46 | 2.54 [15] | 93–94 [23] |
| PEN | 12.78 | 12.73 [16] | 80 [24] |
| PC | 10.82 | – | 68–70 [25] |
| PES | 9.70 | 8.33 [17] | 72 [26] |
| AR | 12.89 | 12.88 [18] | 56 [27] |
| PP | 6.44 | 6.5 [14] | 95 [23] |
| PMMA | 3.15 | – | 73 [21] |
| PVDC | 2.56 | – | 80 [23] |
| PEEK | 13.76 | 10.30 [19] | 70 [28] |
| PVA | 2.70 | – | 36 [23] |

equilibrium of the three phases, into Eq. (2) yields the famous Young–Dupre equation,

$$W_a = \gamma_{LG}(1+\cos\theta), \tag{3}$$

where $\theta$ is the contact angle of the liquid at an equilibrium state. We calculated $W_a$ for all of the polymers using the water contact angle (WCA) values given in Table 1 using the surface tension of pure water ($\gamma_{LG} = 72.88$ mN/m [30]). Meanwhile, the work of adhesion defined in the microscopic scheme is described using the physisorption energy, defined as

$$\Delta E_p = |E_t - (E_a + E_s)|, \tag{4}$$

where $E_t$, $E_a$, and $E_s$ indicate the total energy of the system, the energy of the isolated adsorbate, and that of the isolated substrate, respectively. In the present model, $\Delta E_p$ is equal to the energy needed to remove an adsorbed $H_2O$ molecule from the polymer surface. Thus, the work of adhesion can be given as $\Delta E_p$ divided by the effective area of a unit cell ($A_{eff}$);

$$W_a^c = \Delta E_p / A_{eff}. \tag{5}$$

## 3. Results and discussion

### 3.1. The equilibrium structure of tested polymer materials

Table 1 shows the calculated and the experimental lengths of one repeating unit of the single molecular chain at the molecular axis direction [14–19] and also the WCA [20–28] of the selected polymer materials. Note that the WCA data of PI shows that of PMDA-ODA which has a similar structure to that of PMDA-PDA. It is evident that PTFE has the highest non-wetting property among the polymers examined in this study, while PVA has the highest wetting property. We compared the calculated and the experimental lengths of one repeating unit of the single molecular chain at the molecular axis direction as shown in Fig. 2. The computationally relaxed lengths of one repeating unit of a single molecular chain were in fairly good agreement with those found experimentally, except for the seemingly anfractuous polymers such as PES and PEEK.

### 3.2. Interaction between $H_2O$ molecule and polymer surfaces

The WCA and $\Delta Q_O$ of the thirteen polymers are compared in Fig. 3(a). Recall that the value of $\Delta Q_O$ given for PVDC represents the average value of PVDC1 and PVDC2. It can be seen that polymers with high wettability are associated with large absolute values of $\Delta Q_O$. In particular, the values of $\Delta Q_O$ correspond qualitatively to those of WCA in PTFE, PE, and PP, each of which have a WCA of more than 90°. To investigate the correlation between the values of $\Delta Q_O$ and WCA, $\Delta Q_O$ is plotted against WCA in Fig. 3(b). The relation between $\Delta Q_O$ and WCA of polymer materials is almost linear except for PEN and PET. The distance between the oxygen atom in an $H_2O$ molecule and the polymer surface in the physisorbed states of PTFE is 7.7 Å and that of PVA is −0.74 Å. Here, we defined the distance between the water molecule and the polymer surface as the difference between average value of *x* coordinates of carbon atoms in the polymer surface layer and *x* coordinate of oxygen atom in the $H_2O$ molecule. Fluorine atoms in the PTFE surface layer have negative Mulliken atomic charge. Therefore, the distance between $H_2O$ molecule and surface becomes long due to the electro repulsion between $H_2O$ molecule and the surface layer. While, PVA has many hydroxyl groups, which show an affinity with $H_2O$, in the molecular chain. As a result, the $H_2O$ molecule is physisorbed between PVA molecular chains. Therefore, the distance between $H_2O$ molecule and surface becomes negative. It is seen that absolute value of $\Delta Q_O$ decreases with increasing distance between an $H_2O$ molecule and a polymer surface, since the overlap population between the oxygen atom in the $H_2O$ molecule and the polymer surface should be decreased. Therefore, $\Delta Q_O$ is correlated with the WCA.

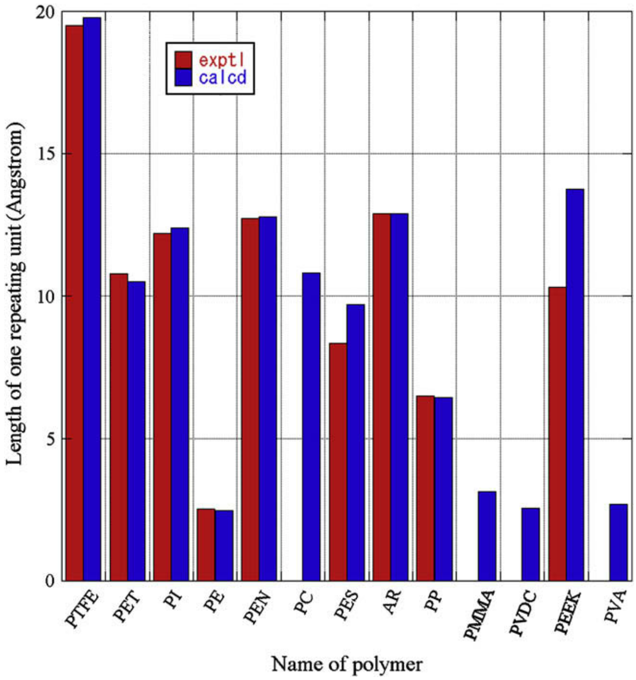

**Fig. 2.** Calculated (calcd) and experimental (exptl) length of one repeating unit of single molecular chain in the molecular axis direction.

### 3.3. Work of adhesion of water on polymer surfaces

The works of adhesion of water on polymer surfaces obtained by Eq. (3) (experimental) and Eq. (5) (calculated) are compared in Fig. 4. As before, the value of $W_a^c$ in PVDC is the average of the values for PVDC1 and PVDC2. The figure indicates the values of $W_a^c$ relative to that of PTFE; i.e., the $W_a^c$ value of PTFE has been subtracted from those of the other polymers, thus the position of PTFE must be zero. The relative changes in the work of adhesion calculated from Eqs. (5) and (3) only agree for PET, PEN and PVDC. However, the relative changes in the work of adhesion calculated from Eq. (5) almost agree with those from Eq. (3) except for PI, PC, AR, and PVA, which show higher wettability (i.e., WCA < 70°).

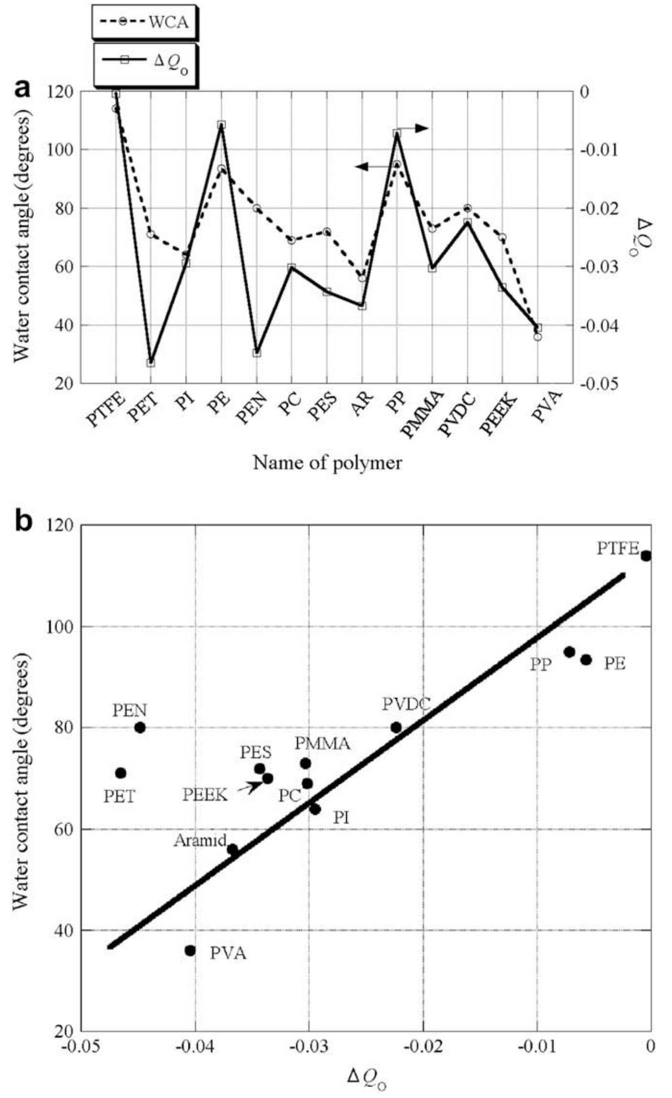

**Fig. 3.** (a) Direct comparison between WCA (experimental) and $\Delta Q_O$ (calculated) of tested polymer materials. (b) Relation between WCA and $\Delta Q_O$ of tested polymer materials. The value of $\Delta Q_O$ in PVDC shows the average value of PVDC1 and PVDC2.

These results suggest that the water non-wettability of the polymer is dominated by the physisorption strength of the $H_2O$ molecule from the microscopic views. Work of adhesion is an ideally reversible physical quantity defined as the work per unit area to dissociate liquid from an inert solid surface. However, when we measure the work of adhesion (or adhesion energy) for receding and advancing contact angles, hysteresis effects are observed between them [31,32]. There is an energy deficit in the total system when the substrate and adsorbate are brought together as defined in Eq. (4). Therefore, physisorption energy between the $H_2O$ molecule and surface can be the origin of the hysteresis effects. If we suppose the physisorption pathway of $H_2O$ molecule on the surface, tensile force should act between surface and $H_2O$ molecule, when $H_2O$ molecule is dissociated from the physisorbed state along the physisorption pathway. Compressive force should act between them, when $H_2O$ molecule is approached to the physisorbed state along the physisorption pathway. Therefore, hysteresis effects between advancing and receding works of adhesion can be explained by these forces driven by the physisorption energy. Also, it can be predicted that hysteresis effects become small when the physisorption energy between the polymer surface and $H_2O$ molecule is small.

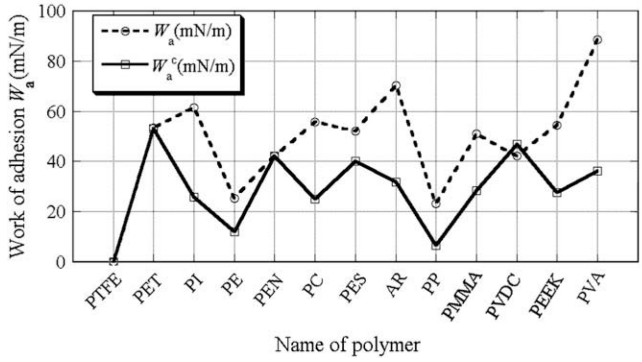

**Fig. 4.** Work of adhesion of water on polymer surfaces obtained from Eq. (3) (experimental) and Eq. (5) (calculated). We employed the values of PTFE as the origin of the figure. The value of $W_a^c$ in PVDC shows the average value of PVDC1 and PVDC2.

## 4. Conclusions

In summary, we have compared the energetic works of adhesion of water onto the surfaces of various polymers by means of the SEMO method using the proposed quantities, $W_a$ and $W_a^c$, defined in both macroscopic and microscopic schemes, and discussed the water wettability/non-wettability of polymer materials. Fairly good agreement between $W_a$ and $W_a^c$ was found in the highly non-wetting polymers. This suggests that there is a strong correlation between $\Delta Q_O$ obtained by the molecular orbital calculations and the phenomenological WCA of the polymer materials. Moreover, physisorption energy between the $H_2O$ molecule and polymer surface can be the origin of the hysteresis effects between receding and advancing contact angles between water and polymer surface.

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