Advanced Powder Technology 21 (2010) 500–505

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Translated Paper

Quantum chemical calculation of electron transfer at metal/polymer interfaces ☆

Yoshiyuki Shirakawa *, Naoto Ii, Mikio Yoshida, Ryusuke Takashima, Atsuko Shimosaka, Jusuke Hidaka

Department of Chemical Engineering and Materials Science, Doshisha University, 1-3 Tatara Miyakodani, Kyotanabe, Kyoto 610-0321, Japan

ARTICLE INFO

Article history:
Received 31 May 2010
Accepted 31 May 2010

Keywords:
Quantum chemical calculation
Contact electrification
Metal/polymer interface
Density of sate

ABSTRACT

Calculation of contact charging at metal/polymer interfaces were performed by a quantum chemical method (DV-Xa). In the calculation, model clusters with dangling bonds were used. The model clusters showed surface states in the density of states (DOS), the electron transfer occurred at the contact interfaces between polymer and Al. Then, 0.3 nm was a reasonable value as the contact distance in the present simulation.

Contact electrifications between PTFE and six metals, such as Pt, Au, Cu, Al, Pb and Ca were simulated. The charge transferred from the metal to PTFE depended on the work function of the metals, and had a gap in range of 4.25–4.28 eV. According to the gap of metals were classified into two groups. If Fermi level of a metal is lower than the lowest unoccupied molecular orbital (LUMO) level of PTFE, the electrons of the metal transfer to the surface state (interface state). Electrons in the other metals with a higher Fermi level move into the conduction band of PTFE.

1. Introduction

Particles in air take charges in powder processes such as mixing, agitation and transport [1]. The particles in microsize or less have large specific surface area, and electrostatic force of the particles for the electrification is larger than gravitational one. It means that particle motion can be controlled by an electric field over the gravitation. Taking advantage of being able to control particle motion by the electric field, electrophotographic systems have been developed as a typical example [2]. The electrophotograph is a visualizing technology of information with charging color particles and widely utilized in information instruments. Carlson method is generally adapted in the electrographic systems, and mainly consists of charging, exposing, developing, transferring, fusing process [2]. For high image quality, high speed printing and downsizing of the present electrographic systems, the development process must be optimized because of the largest size in these five processes and a significant influence on the image quality. In the development process, toner particles obtain appropriate charges, and visualization by the toner particles is performed on latent images of a photoreceptor with opposite polarity to the toner. Then, the design of toner electrification is an important point for precise control of the toner particle behavior. The toner particles are a composite, and polymer material dispersed with pigment, wax and CCA and coated with SiO_2 [3]. The electrification properties depend on many factors. Then, the mechanism or evaluation of main factors of the electrification has to be clarified for the material design of toner particles. As a first step, theoretical approach has been performed in metal/polymer contact electrification. The metal/polymer contacts are a main origin of the electrification in one-component printers. There are lots of researches on electrification of polymers [4–6]. However, the mechanism still has unclear points.

The theoretical investigations of the contact electrification on the polymer materials have been performed by like molecular orbital methods [7–12]. These were by semi-empirical methods and did not take account of surface or interface structures which had different structures from the bulk ones. Therefore, an ab initio calculation based on an interface modeling has been done about the metal/polymer contact electrification in this paper. In our previous papers, charge transfer in Al/PTFE and /PP systems was estimated. For clarification the influence of metals as electron suppliers on the contact charging, the other results of other metals/PTFE can be reported in this paper.

2. Modeling and simulation

Our calculations for estimation of charge transfer at metal/polymer interfaces were based on DV-Xa method [13] of an ab initio calculation. The DV-Xa is one of molecular orbital calculations and can estimate exchange correlation potential of electrons by the electron density. Moreover, reduction of calculation load by

---

☆ Japanese version published in JSPTJ, Vol. 45, No. 6 (2008); English version for APT received 31 May, 2010.

* Corresponding author. Tel.: +81 774 65 6596; fax: +81 774 65 6842.
E-mail address: yshiraka@mail.doshisha.ac.jp (Y. Shirakawa).

0921-8831/$ - see front matter © 2010 The Society of Powder Technology Japan. Published by Elsevier B.V. and The Society of Powder Technology Japan. All rights reserved.
doi:10.1016/j.apt.2010.05.007

sample integral can be performed, and excitation states can be also calculated in the DV-Xa method.

It is thought that contact electrification of polymers is charge transfer phenomenon or charge redistribution in several molecular layers from a surface [14]. Then, modeling of the surface structures is important factor in the present calculation. Most of polymer materials have mixed structures of crystalline and amorphous state. A model cluster of polymer surface could be proposed. The cluster model shows the mixed structure as a combination of parallel and perpendicular direction molecule to a metal surface in a metal-polymer contact. Fig. 1 shows the case of perpendicular contact. As shown in Fig. 1, polymer consisting of 5–6 carbons in a main chain are shorter than real one. However, hydrogen termination is given at the opposite side of metal/polymer interface. Depth of the 5 layer from the interface is enough for electrons redistribution by the metal-polymer contacts. In this paper, electron transfer and electronic structure have been especially investigated in the polymer clusters with the direction of perpendicular to the interface because perpendicular array molecules show largest charge transfer and the charge transfer decreases with decreasing with angle between polymer molecule and metal surface [12]. Therefore, the perpendicular array is dominant structure in contact charging.

Interparticle distance in a particles contact is not less than a repulsive length for interatomic interaction [15]. If the length is the minimum point in the potential energy, it is 0.33 nm in Ar-Ar interaction [16]. Then, it can be assumed that contact distance between particles was more or less 0.3 nm, and electronic states of contacting polymer were evaluated.

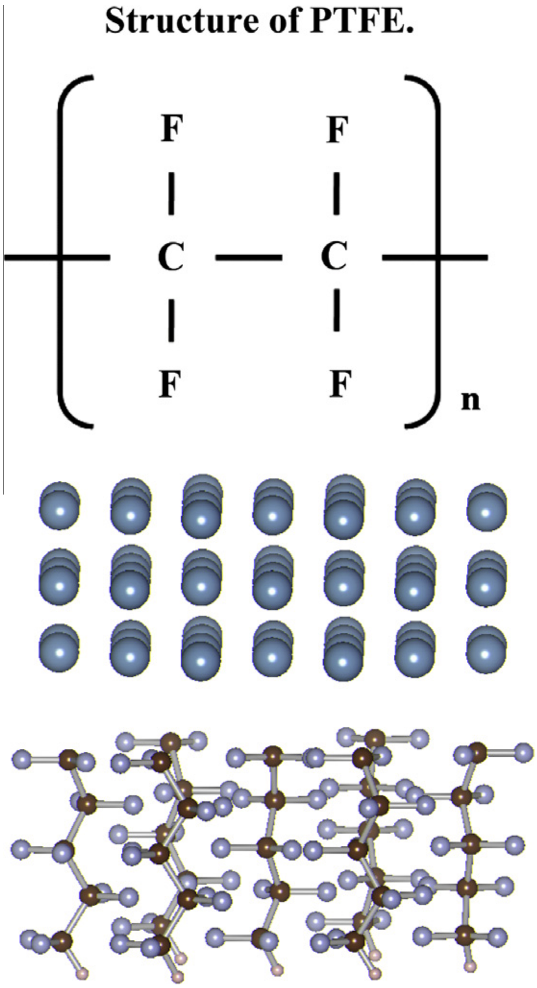

Fig. 1. Model cluster of Al/PTFE.

3. Results and discussion

3.1. Interfacial distance

Charge transfer with changing the interfacial distance between Al and PTFE is shown in Fig. 2. As shown in Fig. 2, the model cluster with 0.3 nm interfacial distance has the largest charge transfer and calculations with more than 0.8 nm distance is over ability of our model. In this calculation, larger charge transfer indicates stronger interaction, and the model calculation can then expressed a lower energy state. Fig. 3(a) and (b) show density of state (DOS) of C2p and F2p orbital in interfacial distances of 0.2, 0.3, 0.4 and 0.5 nm. All profiles of DOS are drown based on 0 eV corresponding to each highest occupied molecular orbital (HOMO) level. In the case of 0.2 nm distance, the profile has an extraordinary shape compared with the other cases and it indicates an unrealistic array model. Therefore, the interfacial distance of 0.3 nm is reasonable, and the following calculations were performed in terms of 0.3 nm distance.

3.2. Influence of dangling bonds on electronic state

The end (C atom) of PTFE molecules faced on the Al surface has a dangling bond which is an electronic state with unbonding electron. Electrons in the dangling bond state are unstable and very active, and affect the contact charging. In our previous paper, the influence of the dangling bonds on the contact charging was discussed from the difference of electron density map between before and after contact [12]. Calculations of DOS were performed for estimation of contribution of the dangling bonds in the contact charging.

Fig. 4 shows three cluster models with changing modification of the end of PTFE molecule. The dangling bonds take a nonactive modification terminated by hydrogen atom in Fig. 4(a). Fig. 4(b) and (c) show a model with bare dangling bond and with the interface between Al surface and dangling bonds. All calculations were performed only about a central molecule in each model. Total DOS based on HOMO level as 0 eV is shown in Fig. 5(a), (b) and (c). The nonactive model has a typical insulator band structure with a energy gap as shown in Fig. 5(a). The energy band in PTFE with the dangling bonds on the surface has a surface state in the band gap (Fig. 5(b)). The HOME level in Fig. 5(c) indicates that electrons transfer from Al to the surface state of PTFE. Therefore, the surface level of the dangling bonds of PTFE has a large contribution to the contact charging. In the case of PP/Al contact, electronic structures change was similar to that of PTFE in the charging.

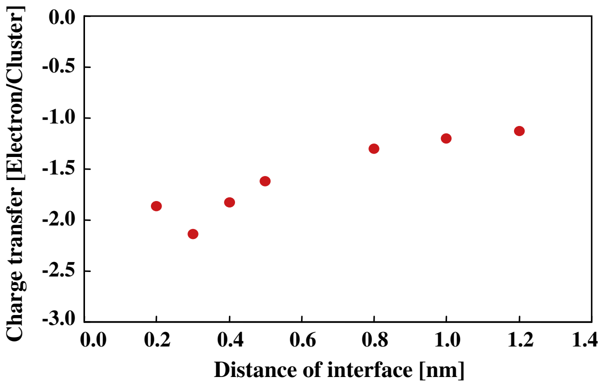

Fig. 2. Charge transfers as a function of the distance of interface (Al-PTFE).