Polybutylene terephthalate on metals: a density functional theory and cluster models investigation

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Abstract
The strength of adhesion of polybutylene terephthalate (PBT) on aluminium is investigated using density functional theory-based energy calculations. The aluminium atom is connected to a PBT monomer at different orientations, and total energies are calculated and compared to determine the most stable orientation. The binding is strongest when the Al is oriented at 180° to the ester group of the monomer. Using this orientation as a basis, PBT adhesion on Ti, Ag, and Au is also investigated.

1. Introduction

Polybutylene terephthalate (PBT) is a strong and highly crystalline engineering plastic which has comprehensively excellent properties such as high impact strength, and has short mould cycles and low moulding temperature. It is a known thermoplastic, and has been studied because of its vast range of applications in the automobile industry, electronics, and electrical appliances [1–7]. Present technologies are being developed for the use of this engineering plastic because of the good thermal stability, excellent chemical resistance and economical availability. One of these technologies is NanoMolding Technology, wherein one uses PBT and PPS (polyphenylene sulfide) to integrate with aluminium in products [1]. Studies have been made of PPS interaction with different metal atoms using density functional theory (DFT)-based calculations [2, 3]. It was shown that PPS binds strongly with titanium, followed by aluminium, and the larger transition metals showed weaker results, when the metal atom was placed next to the sulfur atom of the monomer. However, there are fewer studies on PBT in terms of metallization and most of them are based on spectroscopic measurements. These
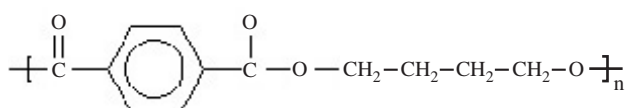
Figure 1. PBT monomer.

1 180° with C=O
2 110° with C=O
3 90° with C=O
4 60° with phenyl ring
5 90° with phenyl ring
6 110° with linking C–O
7 90° with linking C–O

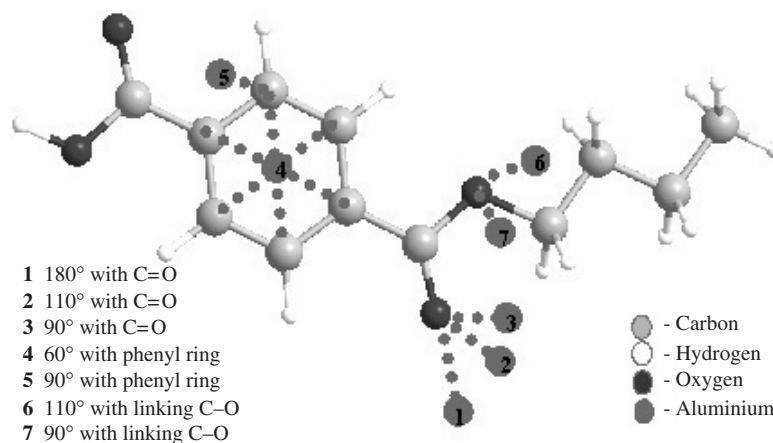- Carbon
- Hydrogen
- Oxygen
- Aluminium

Figure 2. PBT/aluminium model.

studies involve phase transition [5], thermal degradation [6], pretreatment and metallization using KrF-excimer lasers [7], and plasma treatment, on adhesive bonding between PBT and aluminium, which uses some epoxy to improve the adhesion bonding strength [8]. X-ray photoelectron spectroscopy (XPS) results showed that the deposition of an aluminium film preferentially occurs in the carbonyl binding site of the PBT [7]. Similar findings were obtained in studying the adhesion of another polymer, polyethylene terephthalate (PET), and other polymers with C=O components [9–11]. They demonstrated strong interaction between the metals and the ester group.

In this paper, we investigate the adhesion of PBT on metal atoms in terms of the relative stability of the metal/polymer system at the atomic level. In the same manner as for PPS, we consider a model which consists of a PBT monomer and a metal atom that was connected in different orientations. From this model, we examine first the possibilities of the adhesion of Al on the carbonyl, the linking oxygen from carbonyl to the butylene group, and the phenyl group of the PBT monomer. From the calculated total energies, we determine the most stable orientation for PBT on Al, and use Ag, Au, and Ti to further examine the adhesion of PBT on metal atoms. This paper presents a binding mechanism for PBT on metal atoms which leads to a larger scope for investigating PBT metallization. Though the investigation just focuses on the atomic interaction of metal and PBT, this provides a wider perspective on the adhesion of thermoplastics on metal that could be very useful in designing future materials and/or devices.

2. Model and method

We use the model constructed by Chtaib *et al* in their study of polyethylene terephthalate (PET) [12], since PBT has almost the same structure as PET. We add two ethylene groups to form the butylene as shown in figure 1. Hydrogen atoms are also added to terminate the two

Table 1. PBT/Al binding energy at different orientations with equilibrium distance r between O and Al.

| Aluminium orientation	Distance r (Å)	Binding energy (eV)
180° with C=O	1.8	1.40
110° with C=O	1.8	1.15
90° with C=O	1.8	0.80
60° at phenyl ring	3.0	0.34
90° at phenyl ring	2.6	0.23
110° with linking C–O	3.2	0.04
90° with linking C–O	4.0	0.02

ends of the PBT monomer. The monomer is allowed to relax and is connected to an aluminium atom in different orientations as shown in figure 2. The aluminium atom is connected to: (1) the free oxygen on the ester group (C=O) at angles 180°, 110°, and 90°; (2) the linking oxygen at 110° and 90°; and (3) the phenyl ring at 90° and 60°. Total energies are calculated as a function of separation distance, r, between the aluminium atom and the monomer. The orientation that obtained the strongest binding energy is used for the other metal atoms, i.e. titanium, silver, and gold. All calculations are carried out using the software Gaussian03 [13] using the B3LYP functional with 6-31G(d) and LANL2DZ (for silver and gold) as basis sets. Binding energies for the models are obtained from the difference between the energy value for relatively large separation r and the minimum energy of the PBT–metal system. The r dependences of the total energy for the different metal atoms are compared and the binding mechanisms are discussed.

3. Results and discussion

3.1. PBT/aluminium

The total energies as a function of r for the different orientations of the aluminium atom connected to the PBT monomer are shown in figure 3. It can be seen that the minima are found at $r = 1.8$ Å for each orientation, 180°, 110°, and 90° with the C=O of the monomer. The lowest is found when the aluminium atom is linear with the ester group with the binding energy of -1.40 eV. This orientation is almost the same as that of the most stable structures on PET/Al with the C–O–Al angle $\approx 173°$, wherein two aluminium atoms are connected separately to the free oxygen [10]. The next lowest minimum is the one oriented at 110° with the binding energy of -1.15 eV, followed by -0.80 eV at 90° orientation. For the phenyl group, both orientations 60° and 90° are unstable compared to the deposition on the C=O group. It can also be observed that there is no minimum for orientations wherein the aluminium is connected to linking oxygen of the PBT monomer. This indicates that adhesion in these directions is very minimal. The binding energies of the different orientations are summarized in table 1.

The strong binding of aluminium in the 180° orientation is due to greater interactions of the s and p electrons of oxygen and the aluminium. From the orbital population analysis, results show that there are considerable changes in the electron distribution on the 3p orbital of Al, in which the largest change occurs at 180°, followed by 110°, then 90° with the C=O. Moreover, the strong bonding of aluminium to the oxygen in linear orientation can also be attributed to the pi bonding of Al and O on the p orbital. The 90° orientation with C=O is very weak because the lone pair of the pi bonding of O is perpendicular to that orientation. The calculated Mulliken charges show that there are significant charge transfers between the aluminium and oxygen atoms for the first three orientations, indicating that ionic bonding is
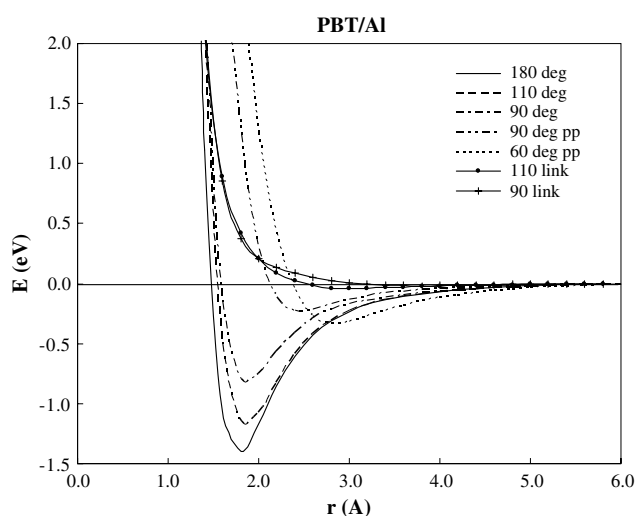
**Figure 3.** Total energies of PBT/Al as a function of r for different orientations.
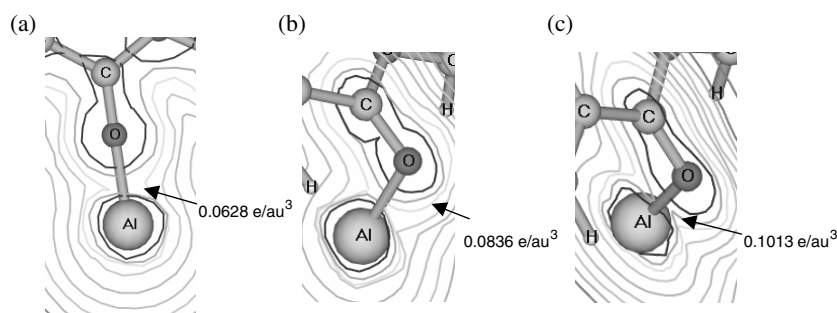
Figure 4. Electron density plots of C, O, and Al for (a) 180°, (b) 110°, and (c) 90° orientations at the equilibrium position $r = 1.8$ Å.

possible, between these two atoms. To further illustrate the occurrence of the ionic bonding, electron density plots focusing on the ester group for the equilibrium position of PBT–Al in the first three orientations are shown in figures 4(a)–(c). It can be seen that the electron density on Al at 180° orientation has the lowest value and the highest is at the 90° orientation, showing greater unequal sharing of electrons between C–O and Al when the C–O–Al angle is increased. These results agree with the observations stated in previous studies on polymer/Al adhesion regarding the ester group and Al [10]. However, when the aluminium atom is placed near the linking oxygen with a group of ethylene on the other end and in the phenyl ring, little charge transfer occurs, and thus the binding between PBT and Al is weak.

3.2. PBT/(Ti, Ag, Au)

The r dependences of the total energy for silver, gold, and titanium are shown in figure 5. It can be seen in table 2 that among the metals used, Ag bonds strongly with a binding energy of 2.08 eV at 2.0 Å, followed by Ti with 0.73 eV at 1.8 Å, and then Au with 0.12 eV at 2.8 Å. It can also be observed that the stable positions of PBT with the metal atoms increase with increasing
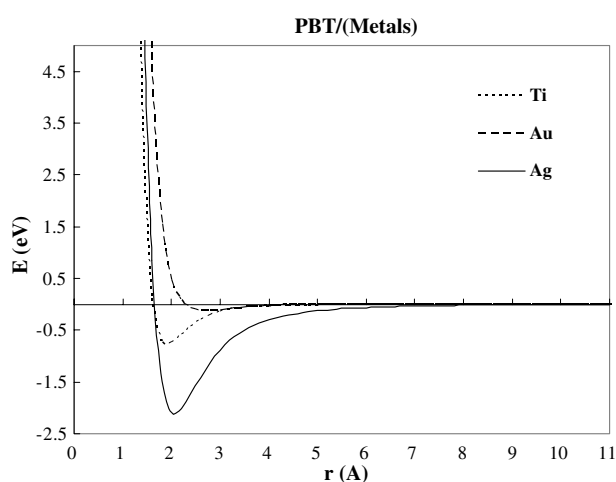
Figure 5. Same as figure 3, but for PBT with Ti, Ag, and Au.

Table 2. PBT binding energy for different metals connected to the C=O of PBT monomer at 180°
at equilibrium distance r.

Metals	r (Å)	Energy (eV)
Titanium, Ti	1.8	0.73
Silver, Ag	2.0	2.08
Gold, Au	2.8	0.12

size of metal atom. The adhesion of PBT to Ti is attributed to interactions involving its d
electrons. From the Mulliken analysis, only the stable positions demonstrate ionic bonding.
In the case of Au, being the larger transition metal, there is a greater ionization energy, hence
resulting in a weaker bond.

On the other hand, the strong adhesion of Ag with the O in the C=O is quite surprising
because, from the result, it has stronger adhesion to PBT than Al. This is attributed to the
covalent bonding between oxygen and silver as a result of hybridization of the p orbital of
oxygen and d orbital of silver. This result is in good agreement with the photoelectron and x-
ray adsorption experimental results from the group of Bukhtiyarov, showing that the formation
of chemical bonds between oxygen and silver atoms results in partial transfer of electron
density from the 4d and 5s orbital of Ag [14]. Moreover, Mulliken analysis shows indications
of charge transfers, enhancing the oxygen–silver bonding in PBT/Ag systems.

4. Conclusion

We have investigated the adhesion strength of PBT on some metal atoms using density
functional theory-based total energy calculations. PBT monomer adheres strongly to an
aluminium atom at 180° with the free oxygen of the ester group. Among the metal atoms Ti,
Ag, and Au, the Au demonstrates the weakest reaction while Ag shows the strongest bonding
with PBT. This study has been conducted on the possible adhesion of PBT with representative
metal atoms from different rows of the periodic table. Further theoretical investigations are
being carried out on other metal surfaces in periodic models to explore potential applications
of PBT–metal adhesion.

Acknowledgments

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