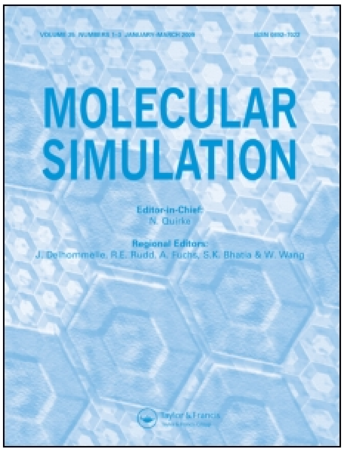

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# Theoretical study of adhesion between graphite, polyester and silica surfaces

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# Theoretical study of adhesion between graphite, polyester and silica surfaces

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This study examines the interaction between graphite and polyester-based polymers and silica in order to compare the adhesive properties of these surfaces. Surface interaction energies were calculated at different interfacial separations, and the resultant adhesion energy curves were used to determine the Work of Separation ($W_{\mathrm{sep}}$) and equilibrium interfacial separation ($d_0$). Adhesion between graphite and polyester was calculated to be significantly greater than between graphite and silica. Our calculations indicate that Van der Waals Forces lead to significant adhesion between graphite and polyester. However, the Van der Waals attraction is approximately 30% less between graphite and silica.

*Keywords*: Adhesion; Work of separation; Van der Waals forces; Equilibrium interfacial separation

## 1. Introduction

Polyester-based polymers have found many important applications ranging from fabrics and paints through to printing toner particles and electrical insulators. However, the long-term durability of these polymers can be affected by exposure to air- and rain-borne pollutants [1–4]. One class of atmospheric pollutant that may affect the performance of polyester-based polymers is carbonaceous solids [5–7]. Polyester surfaces are generally considered to be hydrophobic and may have a relatively high affinity for other hydrophobic materials such as carbonaceous solids. The polymer hydrophobicity arises from the fact that only a limited number of hydroxyl groups are present at the surface with which water can hydrogen bond [5–7].

It has been suggested [8,9] that due to the hydrophilic nature of silica surfaces they may be less susceptible to adhesion of carbonaceous materials than organic polymers. Specifically, the presence of permanent charge and/or the overall hydrophilicity of the silica should produce a poorly adhering substrate for hydrophobic hydrocarbons or carbon-like solids.

The affinity of various surfaces to one another is reflected in the magnitude of their adhesion which can be theoretically characterised by calculating the Work of Separation ($W_{\mathrm{sep}}$) and/or Work of Adhesion for different atomistically represented molecular models of the surfaces in contact [10]. Idealised or typical surface models can be used in computational experiments to obtain insight into the effects of surface chemistries on theoretical adhesion energy, which is a fundamental quantity determining the practical adhesion. Such model experiments have proved to be able to provide fundamental information on the trends in material behaviour that can be used to understand and predict properties of realistic materials [11–13]. In general, forcefield methods allow for modelling of fully atomistic representations of large molecules and structures with several algorithms available to accurately describe condensed phases and surfaces [14–16].

Recent forcefield studies of adhesion include investigations of polymer interfaces and interfacial energies [17–19], the interactions between polymers and single-walled carbon nanotubes [20,21], and investigations of relative interaction energies between synthetic polymer adhesives and cellulose substrates [22–25].

The goal of this paper was to theoretically examine interactions between model surfaces of graphite, polyester and silica in order to determine how the chemical nature of the surfaces affects their adhesion properties.

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## 2. Theoretical procedures

### 2.1 Work of separation

The reversible work required to separate an interface into two ideal free surfaces, with suppression of plastic and diffusional degrees of freedom, is commonly referred to as the *ideal* Work of Separation ($W_{\mathrm{sep}}$) [10]. This quantity can be defined unambiguously and can therefore generally be calculated by theoretical procedures in a relatively straightforward way. However, in experimental cleavage studies, it is not possible to suppress diffusion and relaxation of the surfaces as they are separated. It is therefore difficult to compare directly absolute values calculated for the Work of Separation with experiment. However, $W_{\mathrm{sep}}$ is fundamental to the mechanical properties of the separation of the surfaces like a state function and generally, greater the value of $W_{\mathrm{sep}}$, greater the energy required to separate the surfaces [10].

The Work of Separation can be related to the free energy of the interface ($\sigma_{12}$) and the excess free energies of the individual surfaces ($\sigma'_1$ and $\sigma'_2$, respectively) by the Dupré equation [26]:

$$W_{\mathrm{sep}} = \sigma'_1 + \sigma'_2 - \sigma_{12}. \tag{1}$$

Molecular simulation of the energy change as the isolated surfaces are brought into close contact to form an interface that can be used to approximate the Work of Separation. By performing energy calculations at a range of separation distances ($d$), the adhesion energy at each point ($E_{\mathrm{ad}}(d)$) can then be calculated as:

$$E_{\mathrm{ad}}(d) = (E(d) - \mathrm{E}(\infty))/A \tag{2}$$

where, $E(d)$ is the total energy of the system calculated at interfacial separation $d$, $E(\infty)$ is the total energy at infinite separation and $A$ is the cross-sectional area of the interface (surface area in the $x$, $y$ direction). It is then possible to construct an adhesion curve. The difference between the energy of the contacting phases (well depth $E_0$ of the $E(d)$ curve) and the sum of energies for the free surfaces (value of $E(d)$ at infinite separation) represents the work required to separate the interface into the two free surfaces, i.e. the Work of Separation. The position of the minimum of the $E(d)$ curve ($d_0$) is also important as the equilibrium interfacial separation distance relates to the strength of the created interface.

In addition to the Work of Separation, the tensile strength of the interface (i.e. the stress required for a complete separation), is also of practical interest. The relationship between an applied stress and the interfacial spacing is readily available by taking the derivative of the interaction energy $E(d)$ with respect to the interfacial separation distance. The maximum value of the stress is then the peak interfacial strength ($\sigma_{\mathrm{max}}$). Plots of the applied stress versus separation distance can therefore be obtained.

### 2.2 Interface models

The silica and polyester surface models have been prepared as described below taking into account relaxation effects, while an ideal graphite (1 0 0) surface [27] was used to model the carbonaceous layer. The resultant silica and polyester surfaces were therefore atomically rough and realistically inhomogeneous.

The polyester model (Polyester) was based on the previously obtained system [28]. However, this model was further modified as follows: (a) the partial atomic charges were recalculated using the Charge Equilibration procedure [29,30] and, (b) the model was energy minimised to account for the effects of the new charges.

The silica models used in the present study were based on the work of Garofalini and co-workers [31–34] and have been modified as reported previously [35,36] to produce surfaces with varying degrees of surface hydroxylation. However, in the present study we have further modified these surfaces by redetermining the charges using the Charge Equilibration procedure and then optimising the surface geometry by minimising the energy of the surface hydroxyl groups.

Three silica models were prepared with surface hydroxylation ranging from 1.4 OH groups per nm$^2$ (23 hydroxyl groups per unit cell surface area, Silica23), and 2.2 OH groups per nm$^2$ (35 hydroxyl groups per unit cell surface area, Silica35) through to 3.6 OH groups per nm$^2$ (58 hydroxyl groups per unit cell area, Silica58). These models represent "dry" and more "hydrated" surfaces, respectively [37].

All surface models were created to be approximately the same size with an area of 40 × 40 Å ($x$ and $y$ directions) and a thickness of approximately 18 Å ($z$-direction). The interfaces were formed by different combinations of these surfaces and are listed in table 1. A vacuum spacer was inserted between the pairs of surfaces to represent the interfacial separation. The simulation box was further extended to 300 Å in the $z$-direction to create a vacuum separation in order to prevent interactions occurring across adjacent cells due to 3D periodic

Table 1. Interfaces represented by model systems.

| *System* | *Components* | *Interface modelled* |
|---|---|---|
| 1 | Graphite–Polyester | Carbon-contaminant with polyester |
| 2 | Graphite–Silica23 | Carbon-contaminant with "dry" silica |
| 3 | Graphite–Silica35 | Carbon-contaminant with partially hydrated silica |
| 4 | Graphite–Silica58 | Carbon-contaminant with hydrated silica |
| 5 | Silica23–Polyester | Polyester with "dry" silica |
| 6 | Silica35–Polyester | Polyester with partially hydrated silica |
| 7 | Silica58–Polyester | Polyester with hydrated silica |
| 8 | Polyester–Polyester | Polyester (toner particle) with polyester (photoconductor) |

boundary conditions imposed on the system. As a result, quasi 2D periodic systems were created, where infinite surfaces in contact were mimicked. Subsequent adhesion calculations have been performed between rigid surfaces as described below.

### *2.3 Computational details*

The instantaneous energy at different interfacial separations was calculated for each of the interfaces using the COMPASS forcefield [38]. Partial atomic charges were determined using the Charge Equilibration procedure [29]. The Ewald method was employed to evaluate all non-bonded Van der Waals and Coulomb interactions both for minimisations and for single-point energy calculations with a convergence limit of $4.0 \times 10^{-4}\,\mathrm{kJ\,mol^{-1}}$. Energy minimisation of surface substituents was performed using the Conjugate-Gradient procedure with a convergence limit of $0.04\,\mathrm{kJ\,mol^{-1}\,Å^{-1}}$. System energies were calculated progressively from the largest separation distance to the smallest.

Although all surfaces were created to be approximately equal in thickness (18 Å), the boundary of the interface was difficult to identify (except for graphite) due to the atomic roughness in the surface profiles. The amorphous nature of the silica and polyester surfaces presented an ambiguity in assigning the exact surface boundary; therefore, for the unmodified polyester model it was arbitrarily calculated as the $x-y$ plane having $z$ equal to the average $z$ for all atoms in the leading 2.5 Å of the surface. For the silica models, where the surface substituents increase surface roughness, the boundary was determined to be represented by the $x-y$ plane having $z$ equal to the average $z$ for all atoms comprising the surface modifications plus the atoms in the leading 2.5 Å of the bulk (figure 1). It should be noted that although $d_0$ is directly dependant on the definition used for the surface boundaries, the calculated $W_{\mathrm{sep}}$ is not.

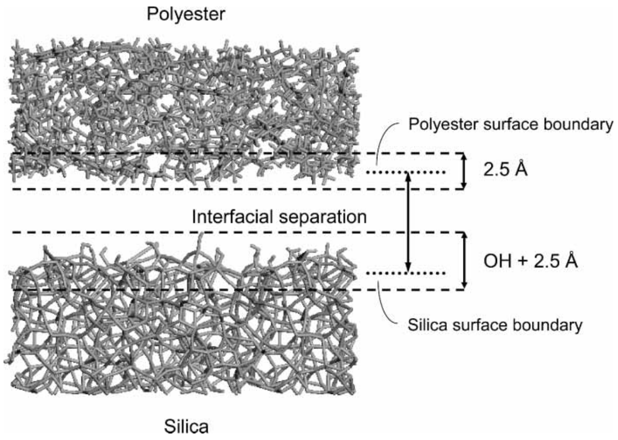

Figure 1. Schematic diagram of polyester–silica interface showing the definition of the surface boundaries and interfacial separation.

## 3. Results and discussion

### *3.1 Adhesion energies*

Table 2 presents key interaction parameters for all interfaces studied, including Work of Separation ($W_{\mathrm{sep}}$), equilibrium interfacial separation ($d_0$), peak width at half-height ($l_{1/2}$), and peak interfacial stress ($\sigma_{\max}$), while figure 2 presents representative adhesion energy curves.

Before discussing each of the individual interfaces in detail, it is useful to make some general observations about the systems. The first point to note is that the strongest interaction occurs between graphite and the unmodified polyester. Noticeably, the interactions between graphite and the various silica models are significantly weaker and relatively insensitive to the degree of surface hydroxylation, while the weakest interactions occur between the polyester and silica surfaces.

As can be seen from figure 2 and table 2, the strongest interaction is predicted between graphite and the unmodified polyester (System 1) and is ~ 30% greater than for the graphite–silica interface. In addition to this, the equilibrium separation for System 1 is ~1.3 Å shorter than for the graphite–silica interfaces. The peak width for System 1 is marginally smaller than for any of the other systems considered and indicates that not only does the maximum adhesion occur at a shorter interfacial separation but also the attraction between the surfaces is significant over a narrow range compared with the other interfaces. This indicates that graphite forms a stronger interface with polyester than with silica at shorter separations, which can lead to a stronger long-term adhesion.

Three silica models were considered in the present study with varying degrees of surface hydroxylation. It is interesting to note that all three silica surfaces give very similar interaction profiles with graphite. The calculated Work of Separation values cover a narrow range and as noted above are ~30% smaller than for graphite with polyester. The equilibrium separations also cover a narrow range and all three peak-widths are ~0.2 Å greater than for polyester graphite. Firstly, these results indicate a weaker interaction between graphite and silica than was observed between graphite and polyester. Secondly, it appears that the interaction between graphite and silica is relatively insensitive to the levels of surface

Table 2. Adhesion parameters determined for Systems 1 to 8.

| *System* | | $W_{sep}=E_0$ *(mJ m$^{-2}$)* | $d_0$ *(Å)* | $l$ *(Å)* | $\sigma_{max}$ *(GPa)* |
|---|---|---|---|---|---|
| 1 | Graphite–Polyester | 118.2 | 3.60 | 1.94 | 0.49 |
| 2 | Graphite–Silica23 | 78.0 | 4.91 | 2.18 | 0.29 |
| 3 | Graphite–Silica35 | 79.5 | 4.92 | 2.18 | 0.29 |
| 4 | Graphite–Silica58 | 82.1 | 4.99 | 2.16 | 0.30 |
| 5 | Silica23–Polyester | 20.7 | 5.26 | 2.40 | 0.07 |
| 6 | Silica35–Polyester | 20.1 | 5.32 | 2.39 | 0.07 |
| 7 | Silica58–Polyester | 20.2 | 5.41 | 2.41 | 0.07 |
| 8 | Polyester–Polyester | 32.5 | 4.04 | 3.40 | 0.06 |

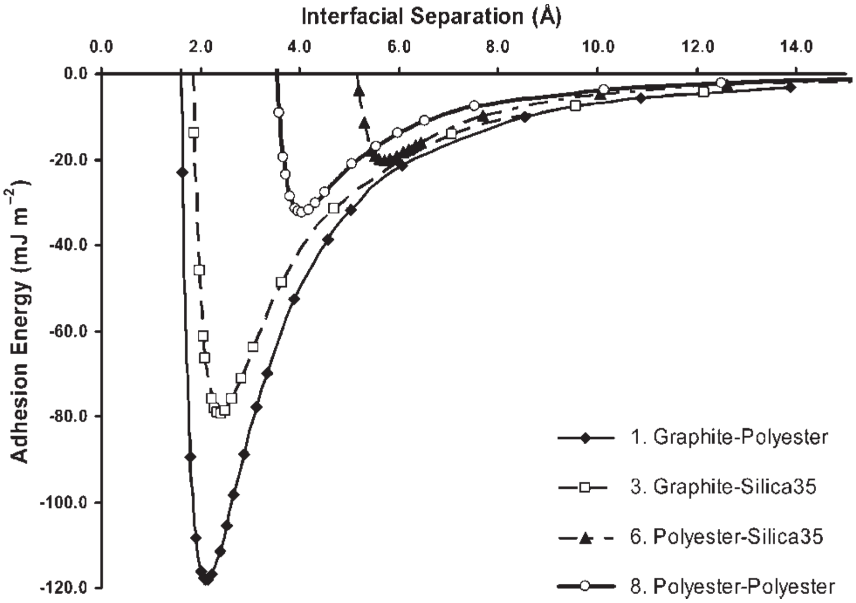

Figure 2. Selected plots of adhesion energy $E(d)$ ($\mathrm{mJ\,m^{-2}}$) versus interfacial separation $d$ (Å).

hydroxylation considered here. These results are consistent with experimental observations [8] of increased resistance to carbon black adhesion by silica, compared with hydrophobic polyester surfaces. It is believed that this could be attributed to the presence of permanent charge on the silica surface, which repels particulate soils and prevents strong adhesion. The surfaces of our silica models do have a net negative charge due to the presence of the OH groups. However, it is important to note at this point that the atoms comprising the graphite model are all identical and therefore to maintain overall neutrality of the graphite structure, do not carry any partial atomic charge. Therefore, the interactions between graphite and the various surfaces in our models are due solely to Van der Waals interactions. Direct comparison with experiment is therefore difficult, however, our results suggest that a weaker Van der Waals interaction also contributes to a reduction of adhesion between carbon particles and silica.

It is useful to note that the Van der Waals interaction energy, between surfaces in vacuum, can be described by the Hamaker equation:

$$W(d) = -A_{12}/12\pi d^2 \tag{3}$$

where, $d$ is the interfacial separation and $A_{12}$ is the Hamaker constant for the interface formed by surfaces 1 and 2 [39]. The Hamaker constant is proportional to the properties of the materials involved and is given by:

$$A_{12} = \pi^2 C_{12}\rho_1\rho_2 \tag{4}$$

where, $\rho_1$ and $\rho_2$ are the atoms per unit volume in surfaces 1 and 2, respectively, and $C_{12}$ is the coefficient in the atom–atom pair potential which reflects the chemical composition of the surfaces. As equation (4) indicates, the Van der Waals interaction energy is directly related to the interatomic interaction term ($C_{12}$) and the atomic densities of the respective surfaces ($\rho 1$ and $\rho 2$), via the Hamaker constant ($A_{12}$). Therefore, if there is a decrease in any one of these terms, provided that the other terms remain constant, we would expect a corresponding decrease in the adhesion energy.

Table 3 presents calculated atomic densities for each of the individual surfaces considered. It can be seen that graphite has the largest atomic density of all of the three types of surfaces, followed by polyester and then the silicas. It can therefore be suggested that one of the factors leading to the weaker adhesion between graphite and silica, compared to graphite and polyester, is the lower atomic density of silica with respect to polyester. Furthermore, the very slight increase in adhesion energy between graphite and the various silica models with increasing hydroxylation may be attributed to the corresponding slight increase in atomic densities of the three silica models.

For the silica–polyester interfaces the interaction is more complex. While both the polyester and silica are overall neutral, the individual atoms comprising the surfaces are charged. Therefore, adhesion between these surfaces will be affected by a Coulomb interaction in addition to the Van der Waals interaction. Interestingly, the Work of Separation terms for Systems 5–7 are not only the smallest of the systems considered but also show even less variation with surface hydroxylation ($< 1.0\,\mathrm{mJ\,m^{-2}}$)

Table 3. Calculated density of individual surfaces.

| *Substrate* | *Density (atoms nm$^{-3}$)* |
|---|---|
| Graphite | 126.1 |
| Polyester | 87.6 |
| Silica23 | 56.5 |
| Silica35 | 56.9 |
| Silica58 | 57.9 |

than observed for the graphite–silica interfaces. However, the equilibrium separations are both larger and cover a slightly larger range than for Systems 2–4.

Several factors may contribute to the significantly lower Work of Separation between polyester and silica. Firstly, the atomic densities of both surfaces are significantly lower than for graphite and should therefore lead to a significantly lower Van der Waals attraction. Secondly, as noted above, the surfaces of the silica models have a net negative charge due to the presence of the OH groups. However, the negative silica surface charge is not counteracted by a similar magnitude positive charge on the leading surface of the polyester. This means that the Coulomb interaction for Systems 5 and 6 is only weakly attractive at the separations for which the Van der Waals force is attractive and, in fact, for System 7 (Silica58–Polyester) the Coulomb interaction becomes repulsive over essentially all of the interfacial separation range investigated. This is perhaps not that surprising since the silica surfaces are hydrophilic and the polyester is hydrophobic.

It must be noted that, relaxation of the interface at equilibrium separation may be quite important for Systems 5–7, i.e. silica–polyester interfaces may have a relatively low Work of Separation term and a higher Work of Adhesion term. This is because relaxation should lead to a decrease in electrostatic repulsions and increase in electrostatic attractions, thus producing a stronger interfacial bond. This is, however, outside the scope of this present study which focuses on the Work of Separation.

Interestingly, Rimai et al. [40] found that the forces required to remove small ($<12\,\mu$m) polystyrene and polyester toner particles from a polyester photoconductor plate appeared to be dominated by Van der Waals interactions. For comparison we have calculated the interaction between two polyester surfaces (System 8) and found theoretically that the polyester–polyester adhesion in our case is also dominated by Van der Waals attraction, i.e. Van der Waals attraction is responsible for 92% of the Work of Separation in System 8 while the remaining 8% is due to electrostatic attraction. This is an interesting theoretical finding that agrees qualitatively with the experimental observations and quite strongly suggests that the most important driving force for polyester–polyester adhesion is Van der Waals attraction.

This finding may have a direct implication for a number of coating systems. For example, in electrophotography, the micrometer toner particles are typically coated with nanometer-size silica particles and several studies have shown that the force required to remove silica treated particles from a polyester photoconductor decreases with silica concentration [41]. Rimai et al. [41] suggested that asperities generated by silica affect toner particle adhesion by altering nonelectrostatic interactions (e.g. Van der Waals interactions). While our model surfaces are overall neutral and therefore do not directly simulate polyester toner particles in an electrophotographic environment, our $W_{\mathrm{sep}}$ results indicate that there is a weaker Van der Waals attraction between polyester and silica compared with polyester to

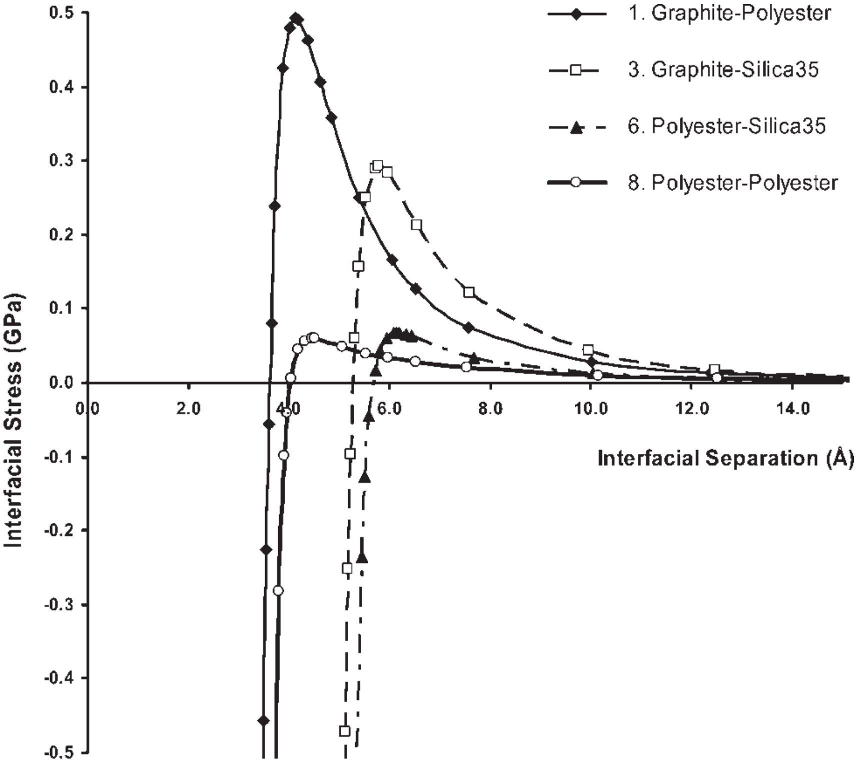

Figure 3. Selected plots of interfacial stress $\sigma$ (GPa) versus interfacial separation $d$ (Å).

polyester. Our theoretical results are therefore qualitatively consistent with these experimental observations that the force to separate two polyester surfaces is greater than that required to separate a polyester–silica interface. Rimai et al. [41] concluded that "asperities in general and silica in particular decrease (polyester toner) particle adhesion for particles in this size range (3.6–8.5 $\mu$m) by reducing the Van der Waals interaction.

### 3.2 *Peak interfacial stress*

The calculated values for the peak interfacial stress ($\sigma_{\max}$) for each interface are presented in table 2, while selected stress curves are shown in figure 3.

The values for $\sigma_{\max}$ generally show the same trends as noted for the Work of Separation. The largest value is observed for the graphite–polyester interface, while the values for the graphite–silica interfaces are $\sim$40% smaller. The lowest values for $\sigma_{\max}$ are predicted for the Silica–Polyester interfaces.

## 4. Conclusions

Our calculations of the Work of Separation ($W_{\text{sep}}$) indicate that adhesion of carbonaceous material (in the form of graphite) to a model polyester surface is greater than to a silica surface. Graphite is predicted to form a strong and tight interface with the polyester surface and a weaker more distant interaction with silica. Adhesion of graphite to silica seems to be relatively insensitive to the level of surface hydroxylation. The theoretical method used here appears to offer a computationally economical procedure for obtaining qualitative results for these adhesive phenomena as well as for investigating the physical nature of the interactions involved. Our calculations indicate that Van der Waals forces lead to significant adhesion between graphite and polyester.

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