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Estimating the Polymer−Metal Work of Adhesion from Molecular Dynamics Simulations

Srdjan Kisin,[†] Jelena Božović Vukić,[‡] Paul G. Th. van der Varst,[†] Gijsbertus de With,[*,†] and Cor E. Koning[‡]

Laboratories for Materials and Interface Chemistry and Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

The thermodynamic concept used to quantify adhesion on a fundamental molecular level is the work of adhesion. However, most of the experimental techniques give no, or very limited information about its magnitude. In this paper, a way to estimate the work of adhesion for copper−(acrylonitrile-butadiene-styrene) (ABS) interface using molecular dynamics simulations is presented. The work of adhesion is calculated from the interactions between single molecules constituting the ABS polymer (poly(styrene-*co*-acrylonitrile) and polybutadiene molecules) and copper (oxide) surface, using their van der Waals contact area. The calculated work of adhesion seems to be independent of the number of polymer molecules present on the copper surface, monomer residue unit sequence within the polymer molecule, and the type of copper surface. Introduction of oxygen atoms to the metallic surface and the polymer molecules significantly increases the work of adhesion. The highest work of adhesion was found between the oxidized copper surface and high oxygen content copolymer poly(styrene-*alt*-maleic anhydride). Results are shown to qualitatively correspond to previously reported experimental observations.

1. Introduction

Adhesion is one of the most ubiquitous phenomena in nature and technology. It is a complex, multifaceted phenomenon, which governs many processes from cell adhesion to biofouling. In technological applications it is important wherever multimaterial systems are used. Since the adhesion strength between dissimilar materials is often inherently poor, it is of specific scientific and industrial interest to study adhesion and adhesion improvement in polymer−metal systems.[1,2]

The thermodynamic concept quantifying the adhesion is the work of adhesion. It combines all the fundamental interfacial forces responsible for adhesion of two different surfaces.[3] Deducing an actual value of the work of adhesion in a system of choice is not an easy task. Most of the mechanical adhesion tests provide largely overestimated values of work of adhesion due to the large energy dissipation originating in the test samples during the measurements.[4] A mechanically measured work of adhesion usually also strongly depends on time and/or temperature.[5] Additional influences of the preparation process in the case of metal−polymer hybrid systems (e.g., metal deposition procedure) have been found on the macroscopic level.

Recently, we have successfully demonstrated[6] that macroscopic mechanical pull-off forces can be qualitatively correlated to substrate−tip interaction forces using nanoscale scanning force microscopy (SFM) measurements. However, even SFM measurements showed a strong dependence of the adhesion properties on the mechanical properties of the polymers,[6] which prohibits the quantitative analysis of the absolute work of adhesion. A possible way to overcome this problem is to numerically simulate SFM measurements using molecular dynamics[7] (MD). This has also been done for JKR measurements[8] but influence of the mechanical properties of the polymers also played an important role here.

To exclude all the described influences and calculate the work of adhesion caused only by the pure physicochemical interactions of the materials, we simulated adhesion of poly(styrene-*co*-acrylonitrile) (SAN) and polybutadiene (pBd) molecules (constituents of the acrylonitrile-butadiene-styrene, ABS polymer) on copper (oxide) surfaces. The choice of the copper−ABS material system was made because it is an industrially interesting combination. The work of adhesion was estimated as the interaction energy divided by the projected area of the molecules' van der Waals volume on the copper surface; the surface is denoted as the van der Waals contact area.

The ABS−copper interfaces are susceptible to morphological and chemical changes. Particularly oxidation of the SAN phase and the copper might strongly influence the work of adhesion. To investigate this, the adhesion of the oxidized

* Corresponding author. Phone: +31 40 247 4947. Fax: +31 40 244 5619. E-mail: G.deWith@tue.nl.
† Laboratory for Materials and Interface Chemistry.
‡ Laboratory for Polymer Chemistry.

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SAN molecule on pure and oxidized copper surfaces was also calculated.

In a previous study[6,9] we proposed a possible way for adhesion promotion between copper and ABS by incorporating the oxygen-containing moieties into a single well-defined block copolymer and use it as an ABS surface modifying agent. Because poly(styrene-*alt*-maleic anhydride) (SMAh) copolymer was identified as a suitable adhesion-promoting molecule, its adhesion properties on copper and oxidized copper surfaces were also simulated and contrasted with the adhesion properties of the SAN and pBd molecules.

2. Computational Methods

We used Materials Studio software package commercially available from Accelrys[10] for all calculations. Force field calculations were performed through the DISCOVER[10] module of the package, using the condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS[10]) force field. Simulations were carried out at a temperature of 298 K controlled by the Andersen algorithm and the equilibration of the structures was performed in the isothermal−isochoric (NTV) canonical ensemble with periodic boundary conditions applied. Duration of the simulations was confined to 50 ps using a time step of 1 fs. The simulation time was confined to 50 ps because within this time period the temperature of the system reached its preset value and no changes of the non-bond and the potential energy of the systems were observed.

2.1. Metallic Copper Simulation. Metallic copper was simulated as a face-centered cubic crystal having unit cell lattice parameters of $a = b = c = 3.6147$ Å. The unit cell was used to create a super cell of 51.1196 × 51.1196 × 20.0000 Å in dimensions from which a (001) surface was cleaved. In the case of surface simulations, the periodic boundary conditions were not applied in the direction orthogonal to the copper surface plane. Only the six topmost atomic layers of copper were allowed to move during the calculations while the coordinates of the remaining copper atoms were fixed. We also added two different copper−oxygen layers on top of the original copper surface, layers containing 0.075 and 0.143 oxygen atoms/Å.[2] The initial configuration of the low-density layer was taken as a (101) Cu_2O plane while for the initial configuration of the high-density layer a (111) CuO plane was chosen. These layers on top of copper surfaces were equilibrated in the same fashion as the pure copper surface, leading to an amorphous structure of about 3 Å thickness on top of the nonperturbed copper surface.

Density and mechanical properties of copper were checked to assess whether the COMPASS force field is suitable for the calculations. Density was estimated at 8.85 g/cm^3, the elastic constants at $C_{11} = 173.8$ GPa, $C_{12} = 99.7$ GPa, and $C_{44} = 102.2$ GPa. With use of the Voigt-Reuss-Hill[11] rule, the calculated polycrystalline Young's modulus was 172.7 GPa and Poisson's ratio was estimated at 0.365. Experimental values are 8.90 g/cm^3 for the density,[12] the elastic constants[13] are $C_{11} = 168$ GPa, $C_{12} = 121$ GPa, and $C_{44} = 75.4$ GPa, following the Voigt-Reuss-Hill[11] rule, polycrystalline Young's modulus is 127.3 GPa, and Poisson's ratio[12] is 0.326.

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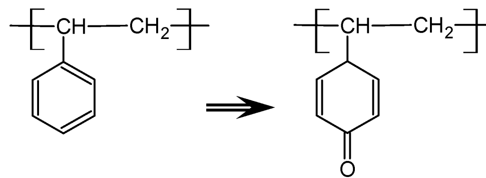

Figure 1. To construct an oxidized SAN molecule, five styrene rings were changed to a quinone structure.

SAN, pBd, oxidized SAN, and SMAh molecules, which were equilibrated in vacuum separately, were subsequently positioned on the top of the previously created copper (oxide) surface and the new structures were equilibrated.

2.2. Construction of the Polymer Molecules. The SAN molecule was constructed as a random copolymer having 20 monomer units, 15 styrene, and 5 acrylonitrile units, a ratio similar to the real material; the pBd was polymerized from 10 1,4-butadiene monomer units and the oxidized SAN was constructed by changing 5 aromatic styrene rings of the original SAN molecule into a quinone structure (Figure 1). In the case of the ABS polymer the oxidation starts in the pBd phase and these changes act as the initiator for further SAN oxidation. SAN oxidation can result in a variety of structures,[14] most of which include the SAN polymer chain scission. To avoid the problem of changing the complete molecular structure, we chose the quinone structure with which to do the simulations. This structure also is a realistic product of SAN oxidation.[15] The SMAh molecule was constructed as an alternating copolymer containing 20 monomer residues.

Note that the commonly used isothermal−isobaric (NTP) ensemble for surface problems simulations was not used in the study since the pressure was not expected to play a significant role in the adhesion of a single molecule on a metallic surface. The NTV ensemble was chosen to keep the basic simulation cell orthorhombic which eases van der Waals contact area calculations. Nonetheless, one simulation of a SAN molecule on a pure copper surface was done under NTP ensemble, using the Andersen barostat to keep the cell orthorhombic. The calculated work of adhesion was found to deviate 3.5% from the one calculated under NTV conditions.

2.3. Interaction Energy and Work of Adhesion Calculations. The interaction energy between the polymer molecule(s) and the copper surfaces was calculated according to the following equation:

$$E_{\text{interaction}} = (E_{\text{copper}} + E_{\text{polymer}}) - \mathrm{E}_{\text{total}}$$

where $E_{\text{interaction}}$ is the interaction energy, E_{total} is the total energy of the copper and the molecule(s) in contact at equilibrium, and E_{copper} and E_{polymer} are the total energies of the copper and the polymer molecule(s) separated in vacuum in equilibrium, respectively.[4] The work of adhesion W_A was calculated as

$$W_A = \frac{E_{\text{interaction}}}{A_c}$$

where A_c is the van der Waals contact area between the molecule(s) and the copper (modified) surface(s). Therefore, with study of more than one SAN molecule, the energy arising from the interactions of the molecules have been taken into account. This energy is contained within E_{total} as well as within E_{polymer}, thus properly taking into account the polymer−polymer interaction.

To calculate the van der Waals contact surface area A_c, we simply plotted the top view of the molecule equilibrium conformation on the copper (modified) surface using van der Waals' radii of all the

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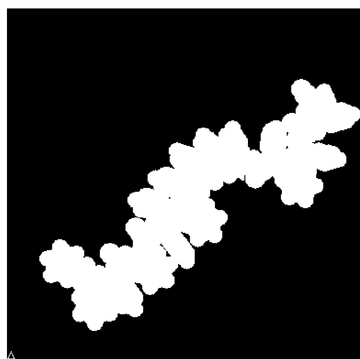

Figure 2. Top view of the equilibrium conformation of SAN molecule on copper (001) surface used for calculation of the van der Waals contact area.

Table 1. Distances between the Top Copper Atomic Layer and the SAN, pBd, and SMAh Molecules (± Denotes the Sample Standard Deviation of the Distances to the Cu Surface of the Atoms within the SAN Molecule)

molecule	distance to copper surface [Å]
SAN	3.62 ± 1.20
pBd	3.20 ± 0.83
SMAh	4.72 ± 1.78

constituent atoms, exported this structure as a bitmap image, changed the color mode of the image to black and white (Figure 2), and determined the percentage of white pixels (molecule). Knowing the dimensions of the system we used, we were able to calculate A_c.

3. Results and Discussion

In Figure 3 a and b, a free SAN molecule close to the copper surface and the equilibrium conformation of a SAN molecule interacting with the copper surface can be seen, showing that the conformation changes significantly.

After 50 ps of MD simulation the molecule has approached the copper surface to an equilibrium distance of 3.62 ± 1.20 Å (Table 1) and, as far as geometrical restrictions[16] allow, the aromatic rings flatten out parallel to the surface. The positions of the aromatic rings are significantly below the average position of the molecule (Figure 4). Apparently, the presence of the copper surface induces the molecule to reorient itself as flat as possible on top of the surface, attracting especially strongly the aromatic rings. Similar observations can be made when two and/or three SAN molecules are present on the copper surface; experimentally, a resembling behavior has been reported for other phenyl-containing molecules on different surfaces.[17] The average distances between the copper surface and pBd and SMAh molecules are also shown in Table 1.

Although the presence of copper influences the conformation of the SAN molecule strongly, the reverse seems not to be the case. As we can see in Figure 5, the standard deviation of the atomic positions within six top atomic layers of the copper surface does not differ significantly whether the surface is in contact with the polymer molecule or not. Even locally, the copper surface retains its vacuum equilibrium structure when exposed to the SAN molecule.

If we calculate the work of adhesion between one, two, and three SAN molecules and the pure copper surface, no differences between the obtained values are observed (Figure 6). The same is true for the work of adhesion between SAN molecules and the oxygen-modified copper surfaces (Figure 6). However, upon oxidation the work of adhesion changes from 0.51 ± 0.02 J/m^2 over 1.47 ± 0.03 J/m^2 to 1.68 ± 0.06 J/m^2 with the increasing oxygen content on the copper surface (0, 0.075, and 0.143 oxygen atoms/Å^2). The copper (oxidized) surface coverage with the SAN molecules goes up to around 80% for the case of three SAN molecules on the surface, so we expect that the work of adhesion will remain the same even if the coverage is 100%. The fact that the work of adhesion of SAN molecules on all three surfaces shows no significant dependence on the number of the polymer molecules suggests that it can be taken as a reliable estimate of the thermodynamic work of adhesion between the bulk SAN polymer and (oxygen modified) copper. All of the mentioned results were obtained by using a copper (001) surface; however, even if a copper (111) surface is used, the work of adhesion of SAN molecules remains 0.51± 0.02 J/m^2. These were the main reasons for which the work of adhesion of pBd, oxidized SAN, and SMAh molecules was calculated only for one molecule on pure copper (001) and the oxygen-modified surfaces.

Furthermore, as shown in Figure 7 the work of adhesion is also independent of the orientation of the SAN molecule on top of the copper surface. For these calculations, a randomly chosen position of the equilibrated SAN molecule on top of the copper surface was taken as a reference position (0° rotation angle), the equilibrated molecule was rotated for a fixed angle as compared the reference position, the rotation was followed by an equilibration step, and subsequently the works of adhesion were calculated. No major changes of the rotation angle prior to and after the equilibration step were observed and thus the work of adhesion is plotted as a function of the initial rotation angle in Figure 7. Since the orientation of the molecule plays no role in the work of adhesion, we expect that different sequences of the monomer residues within the polymer molecule will show the same result, provided that a random distribution of the monomer residues along the molecule backbone exists.

With increasing oxygen content on the copper surface (0, 0.075, and 0.143 oxygen atoms/Å^2), the work of adhesion between the surfaces and the pBd, oxidized SAN, and SMAh molecules increases as well (Figure 8). In the case of pBd on the three surfaces, the work of adhesion increases from 0.42 via 0.93 to 1.13 J/m^2; in the case of the oxidized SAN molecule, the work of adhesion changes from 0.48 over 1.55 to 2.1 J/m^2; for SMAh it goes up from 0.48 via 2.55 to 3.36 J/m^2. Although all four molecules have more or less the same work of adhesion with the pure copper surface (around 0.5 J/m^2, Figure 8 points for 0 oxygen atoms/Å^2), with increasing oxygen content in both interacting parts (copper surface and the molecules), the work of adhesion increases strongly (Figure 8). The highest work of adhesion is achieved for

(16) Angles between the bonds are more or less fixed by the hybridization states of the carbon atoms and only rotation around the single bonds is possible.

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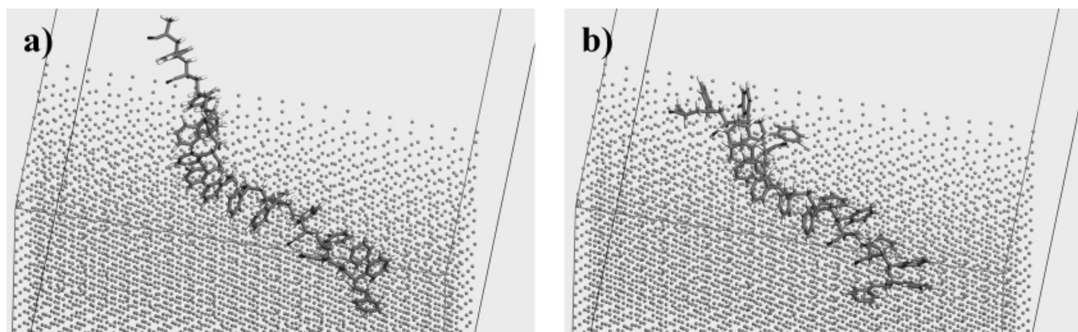

Figure 3. Free SAN molecule close to the copper surface (a) and the equilibrium conformation of a SAN molecule interacting with the copper surface (b). The copper surface used was (001).

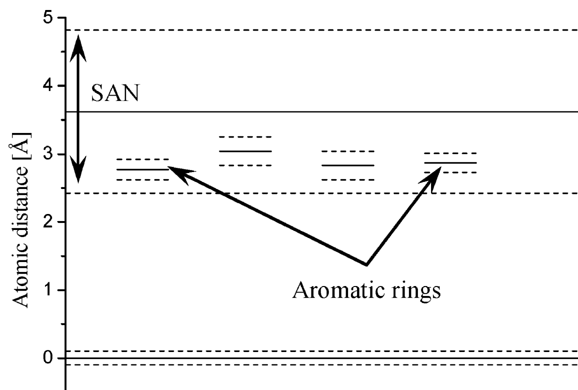

Figure 4. Distance between the top copper atomic layer and the SAN molecule. Solid lines show the average atomic position and the dashed lines indicate the sample standard deviation of the atomic distances (horizontal axis not drawn to scale). Only the aromatic rings oriented parallel to the copper surface are shown; note that not all the aromatic rings present in the SAN molecule orient parallel to the copper surface due to geometric restrictions within the molecule.

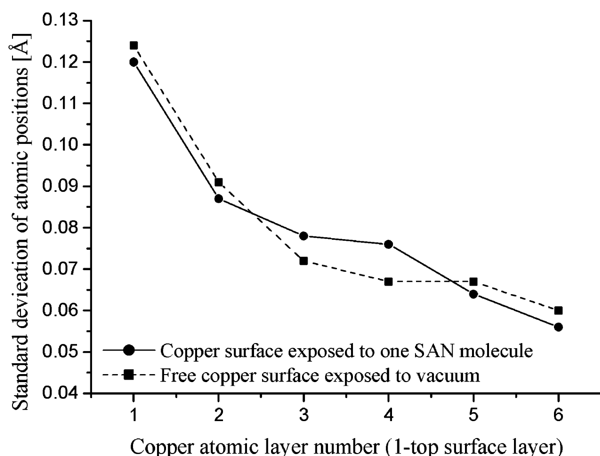

Figure 5. Standard deviations of copper atomic positions within the six topmost atomic layers. Surface in contact with SAN molecule and exposed to vacuum.

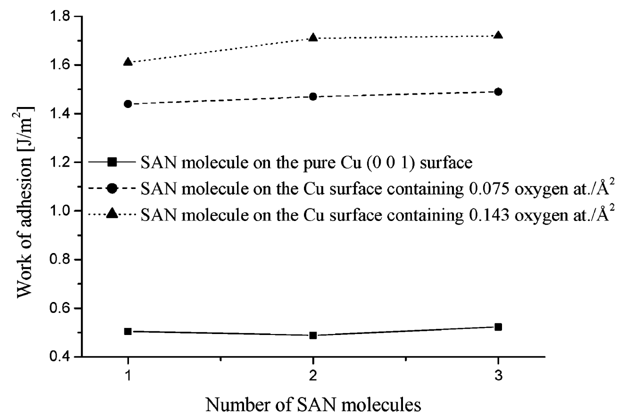

Figure 6. Work of adhesion between SAN molecules and the pure copper surface and oxygen-modified copper surfaces.

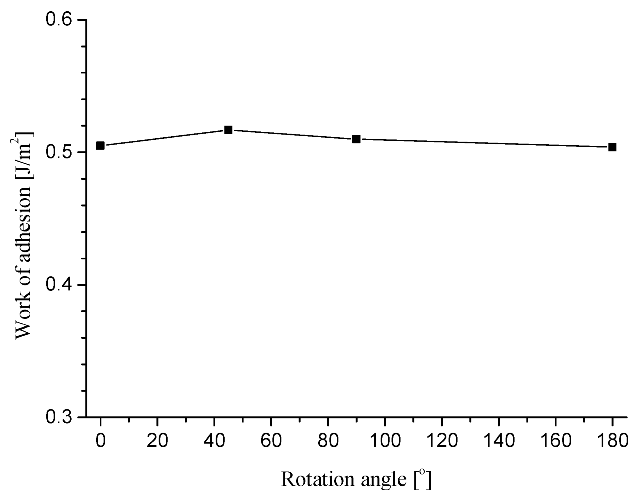

Figure 7. Dependence of the work of adhesion on the position of SAN molecule on copper surface. 0° rotation angle is randomly selected position and the molecule was rotated for preset angles with respect to this position.

the combination of SMAh molecule−copper surface modified with a Cu−O layer containing 0.143 oxygen atoms/Å^2.

Since SAN is the main constituent of the ABS (more than 85 wt %) and SMAh was identified as a possible adhesion-promoting molecule, we shall contrast the adhesion properties of these two molecules in more detail. From the average equilibrium distance of the molecules to the copper surface we note that the SAN molecule approaches the copper surface to a shorter average equilibrium distance as compared to the SMAh molecule, 3.62 ± 1.20 and 4.72 ± 1.78 Å (Table 1) for SAN and SMAh, respectively. We have to mention here that the copolymers interact with copper (oxide) surface(s) via van der Waals and Coulomb forces only, both of which depend on the distance between the interacting parts. This indicates that if the SAN molecule would be on the same average distance as the SMAh molecule, it would exhibit lower work of adhesion. On the other hand, comparison of the average distances is somewhat deceiving as the positions of the lowest atoms within both molecules differ by only 0.3 Å. So the difference in the average distance most probably is caused by the fact that SMAh is a more voluminous molecule as compared to SAN.

When oxygen atoms are introduced to the copper surface as two distinct atomic monolayers with surface density of

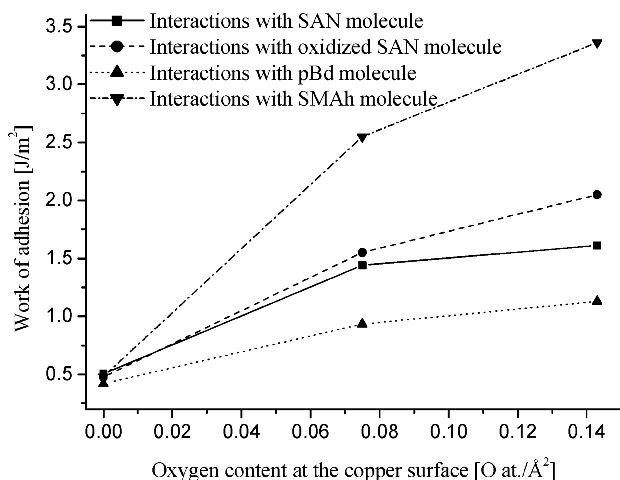

Figure 8. Values for the work of adhesion between single SAN, oxidized SAN, polybutadiene, and SMAh molecule with the pure copper surface and oxygen-modified copper surfaces.

0.075 and 0.143 oxygen atoms/Å^2, the work of adhesion with both molecules increases. It is important to notice that in this specific case the SMAh copolymer shows higher adhesion as compared to the SAN molecule. As seen in Figure 8, modifying the copper surface with a low oxygen density layer leads to a 70% increase of SMAh work of adhesion as compared to SAN (1.44 J/m^2 compared to 2.55 J/m^2), while modification with the high oxygen density layer causes a 2-fold increase of SMAh work of adhesion as compared to SAN (1.61 J/m^2 compared to 3.36 J/m^2).

These findings support the experimental results of macroscopic and nanoscopic adhesion measurements[6,9] where indications of a significantly higher binding affinity of SMAh were found. For both measurements it is realistic to assume the presence of copper oxide on the copper, originating either from the CVD/PVD[18,19] process or due to the fact that the experiments were performed in air.

Since the specific work of adhesion of SAN and the pBd molecules appeared to be independent of the number of molecules present on the copper surface, we can say that the work of adhesion between the ABS and copper can be calculated from the work of adhesion values of the constituent molecules (SAN and pBd) using a mixing rule. There is no difference in the work of adhesion between the SAN and pBd molecules on the pure copper surface, but if the copper surface should contain any oxygen, the SAN part of the ABS will play the dominant role in the adhesion between the two (Figure 8). This is due to the higher interaction energy between the SAN and oxidized copper surfaces and to the larger number of SAN molecules present in the ABS itself. Using oxidized SAN instead of regular SAN will not contribute significantly to the adhesion increase to the pure copper surface but the presence of oxygen in both the SAN molecule and on the copper surface will increase the adhesion strength as compared to the adhesion between the pure components (Figure 8).

As far as the adhesion promotion between ABS and copper is concerned, SMAh does not show any potential for adhesion promotion as compared to SAN when the adhesion to pure, oxygen-free copper is considered. However, a small amount of oxygen is always expected to be present in real PVD/CVD deposited copper layers and thus SMAh seems a very good candidate. Indeed, a strong adhesion increase of PVD-deposited copper films on the ABS substrate treated with a block SAN-*b*-SMAh copolymer was already found.[9]

4. Conclusions

We calculated the work of adhesion between a metal (Cu) and a polymer (SAN) from the interaction of the single molecule with the metallic surface and their van der Waals contact area. The work of adhesion was found to be the same as if calculated from interactions of two or three molecule containing clusters on a metallic surface and is not influenced by the molecular orientation on the surface, the monomer residues sequence in the polymer molecule, and the type of the metallic surface. These results suggest that the work of adhesion thus calculated can be taken as a reliable estimate of the thermodynamic work of adhesion between the polymer and the metal surfaces. In the specific case of interactions between ABS and copper, a separate simulation of the SAN and pBd molecules interactions with the copper can provide insight into the adhesion mechanism. As long as no oxidation takes place, both molecules interact comparably with Cu. Also SMAh and SAN copolymers were found to have a similar work of adhesion on pure metallic copper. However, with the introduction of oxygen at the copper surface, the interaction of SMAh copolymer becomes much stronger as compared to SAN which on its turn interacts more strongly than pBd. The highest work of adhesion of 3.36 J/m^2 was found for the combination of SMAh copolymer and copper surface modified with a Cu−O layer containing 0.143 oxygen atoms/Å^2.

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(18) For macroscopic measurements, copper films were applied on top of the SAN and SMAh copolymer films using physical vapor deposition (PVD), while for the nanoscopic measurements chemical vapor deposited (CVD) copper SFM tips were used to probe the adhesion to SAN and SMAh.

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