

ALUMINIUM/ POLYMERS INTERFACES : CALCULATIONS ON MODEL SYSTEMS AND COMPARISON TO EXPERIMENTS

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INTRODUCTION

The interfaces between polymers and one of the most technologically important metals, aluminium, have been extensively investigated in the context of metallized plastics applications to packaging, decorative coating and electronic devices. In most situations, a strong adhesion between the evaporated metal layer and the polymer substrate is required for the achievement of good mechanical, electrical and chemical properties of the whole system. This adhesion is generally related to the nature of the chemical interactions occurring at the molecular level between the metal and the polymer (0,1,2, 3,4,5,6).

In the present work, we use a tandem theoretical and experimental approach to monitor the first stages of the interfaces between aluminium and various polymers: poly ethylene terephthalate (PET), poly methyl methacrylate (PMMA) and poly styrene (PS). On the experimental level, the interfacial chemistry between vacuum-deposited Al on PET and PS is investigated with static secondary ion mass spectrometry (SSIMS): the gradual growth of the interface was examined "in situ" after every metal evaporation cycle using quadrupole SSIMS and "ex situ" with a time-of-flight spectrometer. Thanks to its high mass resolution a good identification and interpretation of secondary molecular fragments were achieved. Moreover, in order to provide structural informations on the complexes which are formed upon metal deposition, calculations were performed in the framework of the density-functional theory (DFT) (7), within the local density approximation (LDA) (8). As a model molecule, we have studied PET as well as PS chains, consisting of one or two monomers in a box subjected to periodic boundary conditions. Interactions with neighbouring chains were considered by varying the box dimensions while end groups were not considered. After calculations on the isolated PET chain, several Al atoms are introduced in the surroundings of the candidate interaction sites in order to follow the formation of the organometallic complex through the calculation of adsorption energies. We present preliminary results, in which only the interaction with the oxygenated functionalities has been evaluated (phenyl, ester, aliphatic sites should be also considered), and the geometrical configurations were not relaxed. We also evaluate the

changes in the charge density distribution upon metallization. In the case of PS, calculations were done on three different starting configurations which differ by the orientation of the pendant group. We aimed to check the influence of the polymer tacticity on the theoretical density of valence state as well as on the total energy of the system. Although PS has not generally been considered of practical value for polymer metallization, Al/PS interface does offer a model system for a better understanding of the nature of the chemical interaction occurring at the molecular level between a metal and a polymer containing aromatic moieties.

EXPERIMENTAL DETAILS

A complete description of the samples, the SSIMS (quadrupole and time-of-flight) and metal deposition experiments as well as on the experimental conditions (analyses, data treatments) can be found in ref. (3).

THEORETICAL DETAILS

The calculations presented in this study have been performed using DFT as implemented in the Corning Code (9). The Ceperley and Alder electron gas data (10), parameterized by Teter (11), have been used to generate the exchange-correlation energy and potential in the LDA (12). Separable, extended norm-conserving, Ab Initio pseudo potentials represented the ionic cores, following Ref. (13). The wave functions were expanded in a large set of plane waves (12). Special k points were used to sample of the Brillouin zone (12). For each polymer, the Brillouin zone sampling and the number of plane waves was carefully checked. Thus, we obtained a precision of about 0.01 eV on the PET total energy calculations and 0.011 eV for PS. The simulated density of valence state (DOVS) was derived from the PS, PET and Al-PET band structures by convolution of the bare DOVS with Gaussian functions of FWHM = 0.7 eV. This is supposed to mimic solid state effects (i.e. inter-molecular interactions involving the neighbouring chains that cause the broadening of the bands) as well as to simulate the experimental resolution. For Al deposited on PET, we have evaluated the relative stability of different binding configurations from the adsorption energy of the metal atom onto the polymer surface. This energy is defined as follow:

$$E_{\text{[ads]}} = E_{\text{[Al/PET]}} - E_{\text{[PET]}} - E_{\text{[Al]}}$$

In the first PET structure (structure 1), a planar conformation (except the Hydrogen atoms, all atoms are in a plane) has been adopted for the polymer chain with the C=O groups alternatively distributed on each side of the PET backbone. In the second structure (structure

2), we introduced a rotation at the level of the aliphatic part of the chain in structure 1 : the aliphatic segment stays no more in the same plane as the benzene ring. In this second conformation, the ester functionalities remain coplanar with the phenyl ring with the C=O groups on the same side as the backbone of the polymer chain. Two or four Aluminium atoms were then added to the system, to test their interaction with the PET oxygen functionalities. For PS, we have generated the density of valence states (DOVS) for different arrangement of atoms. In short, we analysed one isotactic configuration with one phenyl group per unit cell, contained in a plane perpendicular to the chain, as well as two 'nearly' syndiotactic configurations with two phenyl groups per unit cell.

RESULTS AND DISCUSSION

For PS, the most important cyclic aromatic ions appearing in the PS spectrum (77 Da, 91 Da, 115 Da), together with the metal ion, were followed in-situ upon metallization. As PS typical clusters are characteristic of aromatic entities, the results suggest a loss of aromaticity under metallization. This can be related to the destruction of the aromatic system via an opening of the phenyl rings at the beginning of metallization. This may be due to thermally hot Al atoms impinging on the PS surface. As the energy released by the metal condensation onto the substrate could be responsible of this phenomenon, destruction of the aromatic system can be excluded because the energy released during thermal deposition is low (300-400 kJ / mol) in comparison to the bond dissociation energies of most of the polymers (300-700 kJ / mol). Moreover, if such a destruction mechanism of the aromatic system occurs, strongly unsaturated ions (C₂H, C₂H₂, C₃H₂, C₃H₃, C₄H₂, C₅H₂, C₅H₃ ...) should appear in the metallized PS spectrum. Our results do not evidence such fragments. One may consider a second possibility in which the metal atoms interact directly with the phenyl ring. Thus, a charge transfer takes place and leads to the formation of π -type complex. This interaction perturbs the π electronic system of the phenyl ring which loses its aromatic character and gives rise to diene structures (14).

For Al deposited on PET, the results show a continuous decrease of the PET secondary fragments, associated with an increase of the Al characteristic peak until saturation is reached. This saturation, which corresponds to the deposition of one monolayer, has been correlated to a uniform coverage of the PET substrate as well as to an initial layer-by-layer growth mode (3). The results also suggest that the SSIMS intensity associated to the phenyl ring is strongly affected by the metal deposition. Based on quantum-chemical calculations, Calderone et al. (15) have shown that the phenyl ring can lose its aromatic character in two different ways. Upon Al bonding with the two C=O groups, the phenyl ring may be driven to a fully quinoid character. In that complex, the bond lengths which connect the ester groups to the phenyl ring, shorten from 1.505 Å to 1.384 Å, indicating that the single bonds now present a double bond character.

Furthermore, they do not exclude the possibility of a direct interaction of Al atoms with the phenyl ring. In that case, the phenyl ring loses its aromatic character to give rise to the already mentioned diene structure. The evolution of the sum of the PET characteristic fragments as a function of the Al static SIMS intensity presents a linear relationship with a slope modification around an Al deposited of 4.5×10^{14} atoms.cm⁻². This has been interpreted as the saturation of the carbonyl oxygen able to react with the incoming Al atoms at the surface. Indeed, based on static SIMS results, we compared Al/PET, Al/PMMA and Al/PS interfaces. The results revealed that the growth kinetics decreases from PET to PMMA to PS.

TOF-SIMS analyses were also performed in the high mass resolution mode (HRM) on unmetallized and metallized polymer samples in order to determine peak identity with higher certainty than with quadrupole instrument which have only unit mass resolution. For unmetallized and metallized PMMA and PET samples, the results were published elsewhere (3). For the Al/PS couple, only the peak appearing at mass 163.98 Da [Al₂C₆H₅-(OH)₂] may be attributed to the formation of π -type complex. In the case of both PET and PMMA metallization, the TOF-SIMS results confirmed that the polymer oxygenated functionalities are involved in an interaction with the incoming Al atoms. We also performed a detailed analysis of the oxygen/hydrocarbon isobar components ratio evolution upon metallization. For Al deposited on PMMA, we observed a continuous decrease of all the oxygenated/hydrocarbon ratios while only some of them level down in the case of PET metallization. This result allows one to conclude that all the PMMA oxygen functionalities are attacked by the incoming metal atoms while for PET, the results suggest that some oxygen atoms remain unaffected by the metal deposition even if saturation of the carbonyl oxygen has been reached.

The band structure calculated for the computed DOVS for the first PET structure is such that the 36 doubly occupied valence bands of the virgin PET are essentially flat (maximum dispersion of 0.0267 eV found for band number 9). This feature indicates that the electronic states in PET are highly localised within each unit cell. Chtaïb et al.(16) states that the reason for this localisation originates from the presence of two saturated carbon and oxygen atoms separating the conjugated moieties. To assign precisely the origin of the peak structure in the DOVS curve, we performed a detailed band-by-band analysis of the band structure. We have also generated a second binding configuration (structure 2) on which density functional calculations have been performed. Going from structure 1 to structure 2 does not modify the general shape of the valence band spectra. The most important difference lies in the splitting of about 1.612 eV between band 1 and 2 in the case of structure 1. The molecular levels in this binding region concern the O2s bands involving bands number 1 to 4 built from the bonding (1-2) and anti bonding (3-4) oxygen 2s atomic orbitals. As consequence, the net effect of introducing a 180° rotation between two successive repeat units from structure 1 (structure 2) is to give rise to a degenerated bands 1 and 2 built from the bonding O2s. This feature appears to

bind preferentially to the carbonyl sites for PET and to the carboxylate groups for PMMA. In the case of PS metallization, the results suggest a loss of aromaticity concomitant with the formation of a π -type complex. Furthermore, after saturation of the PET carbonyl oxygen has been reached, we suspect that the incoming Al atoms do not bind to the remaining ether O atoms. On the theoretical level, for PET, we have found that the chain conformation affects the region of the band structure built from the O2s atomic orbitals. Total energy calculations on unrelaxed systems indicates that the Al atoms interact preferentially with the carbonyl oxygen, while interactions with the other oxygen atoms lead to unfavourable situations. For PS, calculations on different chain conformation are in progress. For instance, we observed that the DOVS XPS spectra recorded on PS with atactic and isotactic geometrical conformations are independent on the chain conformation. Comparison with theoretical DOVS should provide more informations.

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