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Metallised plastics waste as a new resource – Study of electronic structure and chemical bond

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Abstract

The use of metallised plastics has increased significantly over recent decades, especially in food packaging, due to the superior performance of these lightweight laminated materials. Currently there is no recycling or treatment solution for these materials. However, these multi-layered plastic and aluminium films can be problematic in plastics or aluminium recycling plants as they can't be readily separated, and so are highly unlikely to be recovered. Hence, they are usually disposed of in landfills or incinerated, imposing a considerable burden on our environment. The aim of this study is to lay the foundations for the development of a new concept for using metallised plastics as secondary resource for industry, thereby overcoming the current limitations of conventional recycling technologies. We investigate the electronic structure and chemical bonding of metallised plastics using microstructure investigation, FTIR, LA-ICP-MS and XPS characterizations and first principle calculations. These results have demonstrated that, there is a strong binding between the metal and polymer at their interface. This makes the recycling of metallised plastic to its components a formidable task. A new process is needed to use them as single component such as in-situ high temperature treatment of these materials to reform metallised plastic to produce high value added components.

1. Introduction

As landfilling and incineration becomes less acceptable due to environmental concerns, space constraints and associated increases in disposal costs, the recycling of complex polymeric waste will no longer be a choice, but an essential future requirement. Metallised plastics are complex multi-layered polymer films which are covered by a metallic aluminium (Al) layer. The deposition of the metallic layer on the plastic surface has gained significant attention due to the superior properties of the various resulting materials and their wide range of uses, especially in the food industry [1]. These multi-layered materials consist of polymeric materials as the base component and coating, as well as metallic layers. Generally, an ultra-thin layer of Al is deposited onto the polymer substrate using a spray or vapour deposition technique, a process called metallising. Then, a coating containing colour will cover the Al layer [2]. Besides providing an effective barrier to atmospheric gases and aromas, metallising also prevents exposure to light and has a high strength-to-weight ratio [3]. Metallised plastics are a better and much cheaper alternative to laminated plastics for food packaging. The thin layer of Al increases barrier properties to moisture, air and odours [4].

As most polymeric surfaces are inert and have low surface energy they do not have the specific surface properties needed to bond to the metallic layer in the metallisation stage [5, 6]. Hence, surface modification is often performed to increase adhesion of the metallic layer, which in most cases in Al, to the polymeric surface. One of the techniques is to use silicon (Si) as the binding element between the Al and the polymer [7]. In the current study existence of Si has been confirmed via elemental analysis on metallised plastic sample and Si has been chosen as surface modifier to bind Al with polymer. After the metallisation step, the metallised plastics will be coloured based on their intended application. Pigments are one of the most important parts of this colouring layer. The colouring layer has three main functions: to provide the desired colour, to protect the

surface and to help the binder in the colour to stick to the surface. Pigments are organic or inorganic tiny solid particles, usually less than 1μm. To reflect light, they must be uniformly dispersed with the solvent on the surface. One of the most important and widely used inorganic pigments is titanium dioxide (TiO2). The fine particles and the strong tinting effect of TiO2 result in improved elasticity and durability of the colour [8].

The recent New Plastics Economy report (World Economic Forum, 2016) [9] noted some USD 80 to 120 billion is lost annually to the world economy in discarded plastic resources, including metallised plastics. After a short first-use cycle, only a global average of 14% of the various plastics thrown away are collected for recycling – most of which are recycled into lower value, lower quality materials. Some 32% of plastic packaging escapes collection systems altogether leaking into the global environment in cities, natural ecosystems and into the ocean. The report [9] estimated the cost of such leakage to the environment and the greenhouse gas emissions associated with plastics production at USD 40 billion annually. However, plastics offer such unrivalled properties and functionalities at such low costs that their use continues to rise steeply. Over the past 50 years, plastic use has increased twenty-fold and the volume of plastics used worldwide is expected to double again within twenty years. One of the fastest growing forms of packaging aremetallised plastics. For example, the packaging industry is expected sharp growth in metallised plastic pouches as consumers choose their convenience and portability over traditional glass, paper, metal and rigid plastic packaging. Global demand for such flexible, multi-layered packaging is projected to rise 6.2% annually to $37.3 billion in 2018 [10]. While the New Plastics Economy noted metallised plastics had some environmental advantages, including preventing food spoilage and waste, and lower emissions associated with transport due to their light weight – they cannot currently be included in plastics collections for recycling. Although the Al and polymer films in metallised plastics are individually recyclable, in their composite packaging formats they are not cost effective to recycle and are destined for landfill, incineration or leakage into the environment.

This has numerous disadvantages; in addition to the direct, negative impact on the environment, is the waste of the potentially valuable resources embedded in metallised plastics, such as Al, C, Si and Ti. Carbon-bearing waste in the landfills leads to release of greenhouse gases, including huge amounts of CO_2 and methane. Up to 50% of the emission is of methane, which is 21 times more potent a greenhouse gas than CO_2 [11]. In addition, landfills can only be sited in specific geographic areas and take up valuable space in densely populated areas. As this complex waste stream accumulates worldwide it represents both a future environmental problem and potential source of untapped secondary resources.

The aim of this study is to investigate the structure of metallised plastics at the atomic level and to develop an understanding of polymer-metal interfaces in these structures. This understanding is essential for the development of a new concept for reusing metallised plastics to produce value-added components through in situ high temperature transformation. In this study, the chemical properties of a waste crisps bag -- as a metallised plastic sample -- were evaluated using different techniques; Fourier transform infrared spectroscopy (FTIR), Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS) and X-ray photoelectron spectroscopy (XPS). Then, using density functional theory (DFT) [12] based on the plane wave-pseudopotential approximation, as implemented in the Vienna ab initio simulation package (VASP) [13], we modelled the deposition of a polymer on an Al metal surface to study its bonding and interaction at the interface. DFT is one of the most successful theories for an ab initio description of materials' properties. It has been used for a variety of applications ranging from the determination of structural properties to electronic properties, and provides results that are in good agreement with experimental studies. In this work, we used the DFT method to optimize the geometry of the deposited molecules on the Al surface and to determine the electron redistribution in the system upon deposition of the molecules and to analyse the density of states of the system, to enable us to discuss the nature of the bonds.

This study aims to establish the basic knowledge essential for developing new techniques such as in situ high temperature transformation for recycling metallised plastics as secondary resources and for enhancing the use of metallised plastics waste beyond traditional landfilling.

2. Experimental details

2.1.*Characterization techniques*
To investigate the structure and thickness of each layer in the metallised plastics, a cross section of the sample waste was studied using optical microscopy and scanning electron microscopy (SEM). The chemical composition of the surface of metallised plastics was analysed using semi-quantitatively Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). To identify the polymer type in the metallised plastic, Fourier transform infrared spectroscopy (FTIR) analysis of metallised plastics was performed on Perkin

Elmer Spotlight 400 FT-IR fitted with attenuated total reflectance (ATR) crystal. The spectrum range was set to 4000 – 650 cm−1. A total of 24 accumulated scans were performed. The carbon chemical states and chemical bonds of carbon in the metallised plastic sample were investigated using X-ray Photoelectron Spectroscopy (XPS) ESCALAB250xi equipped with mono-chromated Al radiation (Kahv=1486.7 eV).

2.2 *Theoretical method*

We performed first- principles calculations based on density-functional theory with VASP [12] in the generalized gradient approximation (GGA) [14], with projector augmented-wave (PAW) pseudo-potentials. The cut-off for the kinetic energy was set to 400 eV and Γ centred grids was used to sample the Brillouin zone.

The Monkhorst–Pack method [15] was used to set the k-point mesh. Using a k-point mesh of $21\times21\times21$ for the primitive cell of FCC Al, and a force convergence criterion of 1 meV/Å, the equilibrium lattice parameter of FCC Al was determined to be 4.05Å, which was in excellent agreement with experiment [16]. A slab of six Al layers consisting of 108 atoms was considered (3x3 supercell) in a supercell with periodic boundary conditions and the polymer was deposited on the Al (100) surface. Crystallographic orientation of polycrystalline aluminium film deposited on each surface is highly dependent on the roughness and structure of the surface underneath [17]. It has been demonstrated that (100) orientation is the dominate orientation of aluminium film deposited on polymer surface at initial stage of deposition [17]. For all the structures, we use a vacuum of 10 Å heights in the supercell to prevent interactions in adjacent supercells in the z direction. All the atomic positions were allowed to relax, except the bottom two Al layers which were fixed to ensure the in-plane lattice constant was equivalent to that of bulk Al. The systems were relaxed until the atomic forces were smaller than 0.01 eV/°A.

The binding energy is defined according to

$$E_b = E_{Total} - (E_{Al} + E_d)$$

where E_{Total} is the total energy of the system containing Al and the deposited atom or molecule, E_{Al} is the total energy of the Al slab, and E_d is the total energy of the free deposited atom or molecule in a large supercell with the same dimensions as the first two terms.

The charge density difference within the system is obtained as follows:

$$\Delta\rho = \rho(Al + Si + P) - \rho(Al) - \rho(Si + P)$$

where $\rho(Al + Si + P)$ is the electron density of Al slab with a polymer deposited on its surface with a Si binding, $\rho(Al)$ is the electron density of Al slab and $\rho(Si + P)$ is the electron density of an isolated polymer attached to a Si atom in the same supercell as the first two terms.

The isosurface map of the charge density difference is visualized in the real space which shows the electronic rearrangements in presence of the deposited polymer.

3. Resulats and Discussion

3.1. *Material characterization*

In this study, the presence of Si as a surface modifier and Ti as pigment in colour was confirmed using the LA-LCP-MS technique. This technique uses the laser abrasion which analyse very thin layer of the surface of the material at its cross section. Table 1 shows the percentage of Al, Si and Ti in the metallised plastic sample; the remainder of the sample was made up of carbon and hydrogen in polymer chains. The structure of the metallised plastic and the thickness of each layer were investigated using optical microscopy and electronic scanning microscopy. As shown in Fig. 1 an Al layer of 5 μm thicknesses was deposited on a polymer layer. Another polymer layer containing colour was deposited on the other side of Al. Each polymeric layer is around 10 μm thick.

To identify the polymer in the metallised plastic structure the sample was analysed using FTIR. Fig. 2 shows the FTIR results. In the wavenumber range around 2950 to 2800 cm−1, the apparent intense peaks can be attributed to the asymmetric and symmetric stretching vibrations of the methyl group of Polypropylene (PP), while the two small peaks adjacent are due to CH2 asymmetric and symmetric stretching vibrations, respectively. The strong peaks at 1500 cm-1 are the result of CH3 asymmetric deformation vibrations or CH2 scissor vibrations, while the peak at ~1380 cm−1 is due to CH3 symmetric deformation vibrations. The C-C asymmetric stretching caused the peak formed at ~1100cm-1, while the peaks below the range of ~1000 cm-1 were mainly due to CH3 asymmetric rocking, C-C asymmetric and symmetric stretching, and CH2 asymmetric rocking vibrations [3].

Table 1: LA-ICP-MS results for chemical composition of metallised plastic

Elements	Al	Si	Ti	C and H
Percentage (wt%)	2.06	1.16	0.88	rest

Further, XPS analysis was conducted to study the chemical state of the carbon in the metallised plastic. The C 1s signal of the XPS spectra is presented in Fig. 3. The main peak was observed at ~284.8 eV, which originates from the C-C bonds, while the peak at ~284.4 eV can be attributed to the C-Si bond which shows the surface modification of polymer using Si. The Si on the surface of the polymer creates a binding environment between the polymer and Al layer during the metal deposition stage. With this surface modification, good surface binding between the Al and polymer will be achieved, as indicated in SEM image in Fig. 1.
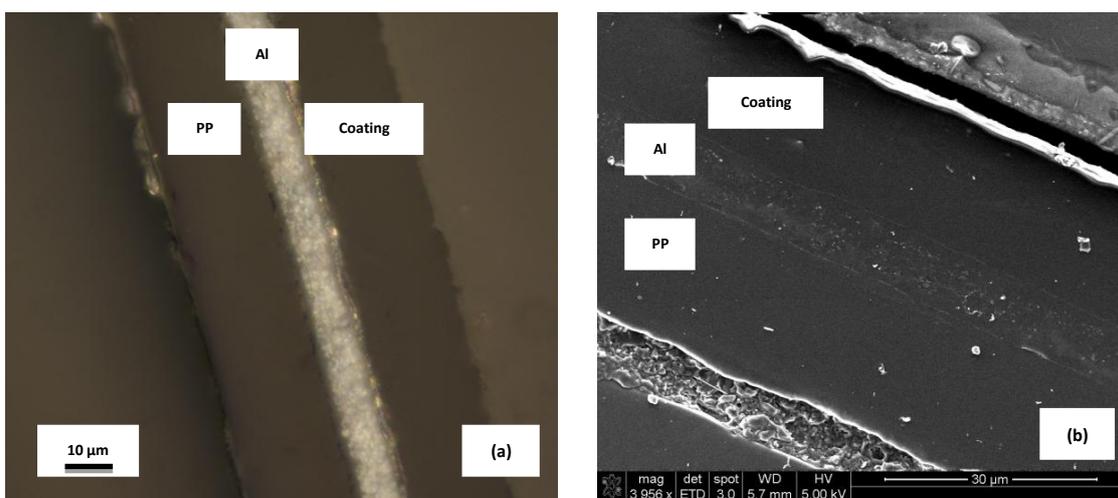
Figure 1: Metallised plastic structure, a) Optical microscopy and b) scanning electronmicroscopy
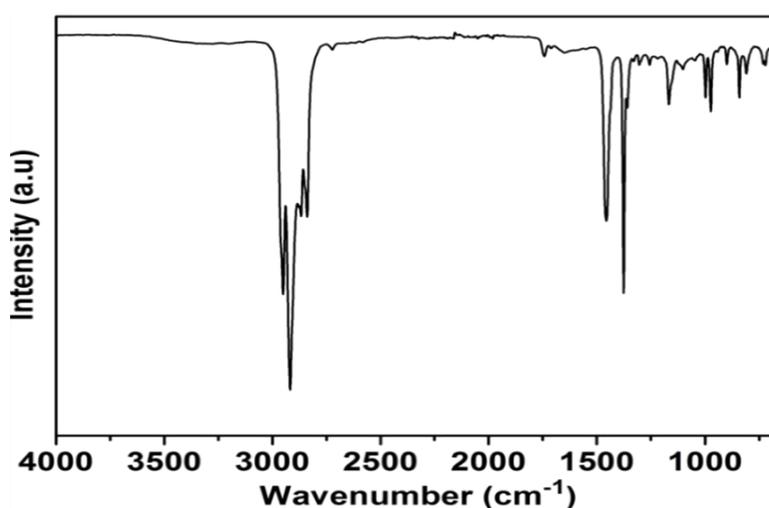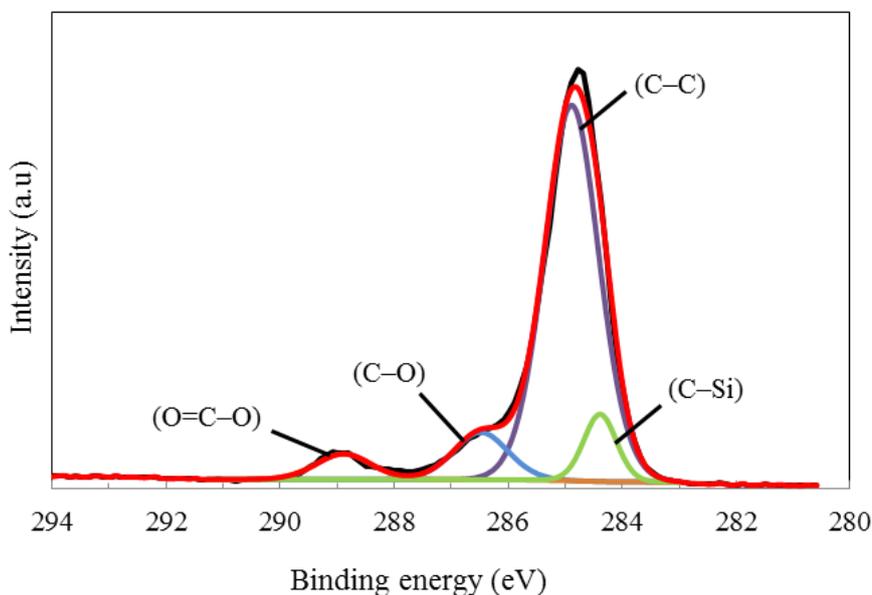

**Figure 2:** FTIR spectrum of metallised plastic

3.2.Theoretical simulation results

To further investigate the bonds at the metal-polymer interface, we perform DFT calculations for a PP chain deposited on the Al surface with Si binding, in both the presence and absence of the colour pigment. To avoid unnecessary complications in the calculations we studied the polymer-metal bond on one side of the Al surface. First, we examined the preferable binding site of Si on the Al (100) surface. We relaxed structures of one Si

atom deposited in three different positions on the Al (100) surface: top, bridge, hollow. Figure 4 shows the position of the top, bridge and hollow sites on the Al surface. Calculations showed that the binding energy of Si is 4.26, 4.75, and 5.42 eV for the top, bridge and hollow sites, respectively, which indicate that the most favourable site for the binding of Si on the Al (100) surface is the hollow site. In this position, Si binds with four Al atoms on the surface. The nearest Al-Si bond length is 2.60 Å in hollow site, while it is 2.36 and 2.46 Å for the top and bridge sites, respectively.


**Figure 3:** FTIR spectrum of metallised plastic
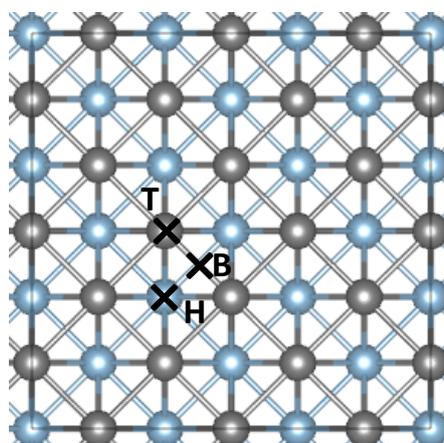
Figure 4: The structure of Al (100) surface of FCC Al lattice from the top view. T, B and H show the position of the top, bridge, and hollow absorption sites, respectively. Grey shows the surface atoms, while other Al atoms are shown in blue.

In the next step, we relaxed the structure of the PP deposited on the Si in the hollow site on the Al (100). Figure 5(a) shows the relaxed structure. The binding energy of Si-PP to the Al surface is 3.79 eV. The nearest Al-Si bond length changed to 2.54 Å after the deposition of the PP. The Si-C bond was 1.91 Å and the C-C axis closest to the Si was tilted by 66°, with respect to the normal Al surface. To further examine the interaction at the interface, we calculated the charge density difference within the system, which plots the redistribution of charge in the system relative to isolated Al (100) and isolated Si-PP. Figure 5(b) presents the charge density isosurface. In this figure, blue and yellow represent charge depletion and charge accumulation, respectively. It can be clearly noticed that charge depletes in Si and accumulates on the Al surface. This charge redistribution indicates that the charge transfer is from the polymer (PP) deposited on the Al surface.
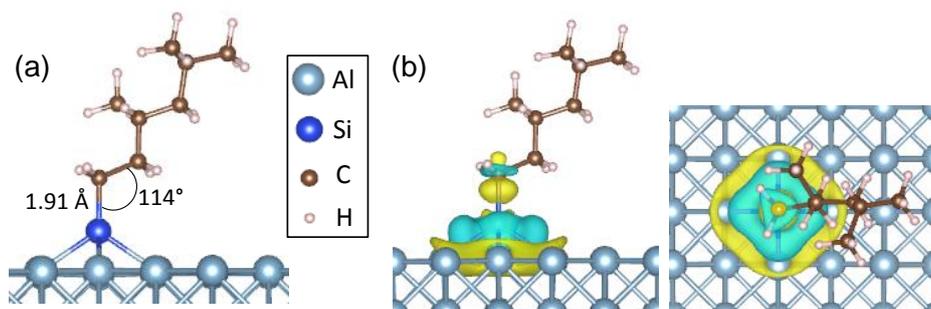
Figure 5: (a) Relaxed structure of PP deposited on the Al (100) surface on Si in the hollow site, (b) charge density difference isosurface of the Al-PP interface from side view (left) and top view (right). Blue corresponds to charge depletion and yellow to charge accumulation. The isosurface value is 5x10-3 e/Å3.
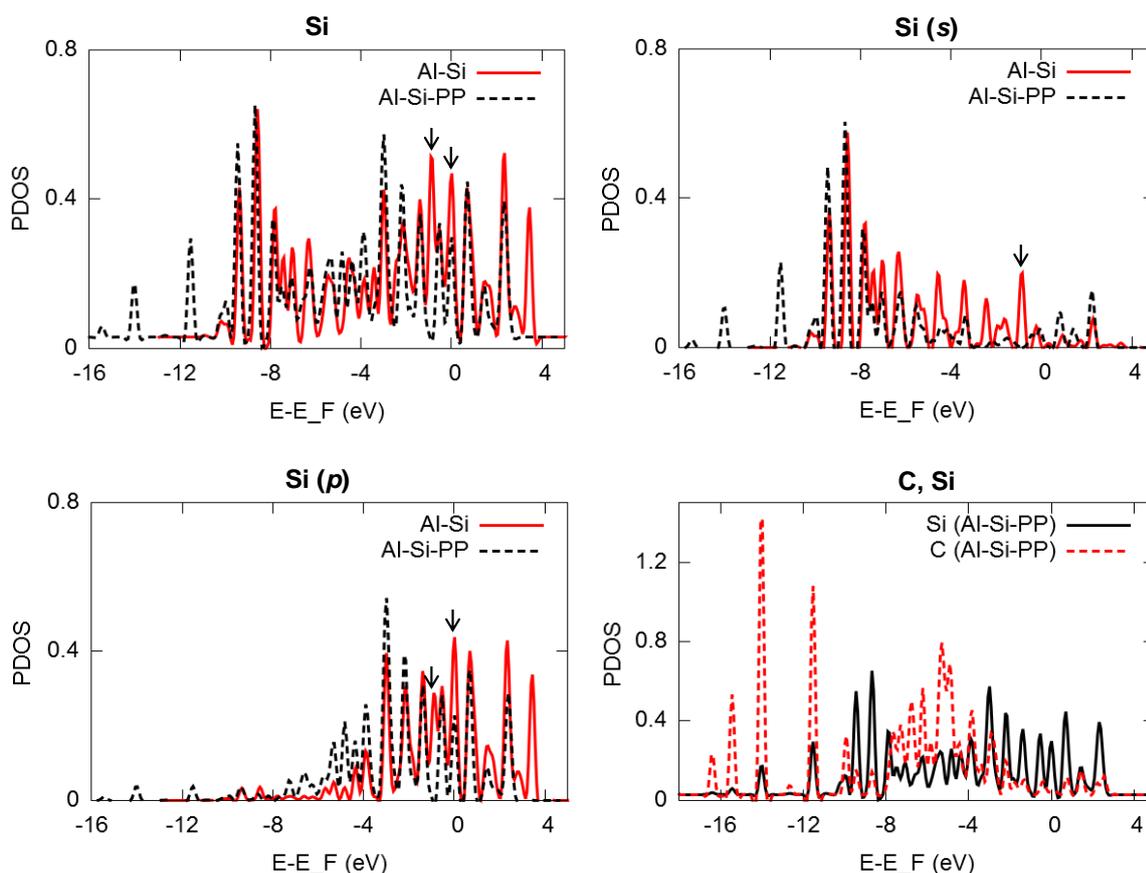

Figure 6: PDOS of Si in Al-Si-PP and in Al-Si. (a) total, (b) s orbitals, (c) p orbitals; and (d) PDOS of Si and the C in PP attached to Si in Al-Si-PP structure. Fermi level is set to zero.

In addition, we compared the partial density of state (PDOS) of the Si-PP deposited on the Al with that of Si on Al. Fig. 6 shows the PDOS of Si in Al-Si and Al-Si-PP structures as well as the PDOS of the C atom in the PP attached to Si in the Al-Si-PP structure. The PDOS results show that Si loses electrons at Fermi level after the deposition of PP in the Al-Si-PP structure (Fig. 6(a), shown by the arrow). According to Fig. 6(c), the PDOS of p orbitals decreases at Fermi level, while it increases at energy levels of between -1.5 and -8 eV. According to Fig. 6(b), the PDOS of s orbitals decreases between -0.5 and -7.5 eV, while it increases at energy levels below -10 eV. The increase of PDOS at energy levels below -10 eV is due to bonding of the Si with the C in the PP. The PDOS peak at -0.9 eV disappears for the both s and p orbitals of Si, as shown by the arrows in Fig 6(a)-(c). This modification in the PDOS of Si after the deposition of PP on the surface is due to the hybridization of Si with the C in the PP, as can be noticed in Fig. 6(d). However, the PDOS of Al is not affected significantly by the deposition of PP.

Next, we considered a structure in which a Ti3O6 cluster was deposited on the Al-Si-PP. For this purpose, we considered two Si-PP on an Al (100) surface and placed a Ti3O6 cluster as a bridge on top of the two PP chains. We relaxed four structures with four different bonding conditions between the Ti3O6 and the PP. For three of the structures the distance between the Si atoms was 4.30 Å and the Ti3O6 was bonded to the two PP chains through (i) two O atoms, (ii) two Ti atoms, and (iii) one O and one Ti atom. For the fourth structure the distance between the Si atoms was 5.70 Å and the Ti3O6 was bonded to the two PP chains through two O atoms. The structure with the minimum energy was structure iii with Ti3O6 bonded to PP through one O and one Ti atom. The other three structures were 1.14, 1.31 and 1.38 eV higher in energy, respectively. However, the strength of the bond between Ti3O6 to PP may vary depending on the distance between the PP chains, their density on the surface and the tilt angle. Fig. 7 shows the relaxed geometry of the structure with the minimum energy and the fourth structure with larger Si-Si distance.

In the minimum energy structure, the binding energy of the Ti3O6 to the Al-Si-PP was 7.5 eV. The C-O bond length between the Ti3O6 cluster and the PP was 1.43 Å, which is in excellent agreement with the experimental value for a typical C-O bond [18]. The C-Ti bond between Ti3O6 and the second PP on the other side was 2.09 Å. The Si-C bond length between the PP and Al surfaces increased slightly (1.92 Å) after attaching the Ti3O6 to the PP chains. The PDOS of Si was not significantly affected, as expected, and only minor adjustments of the PDOS peaks were observed near Fermi level at around -9 eV.
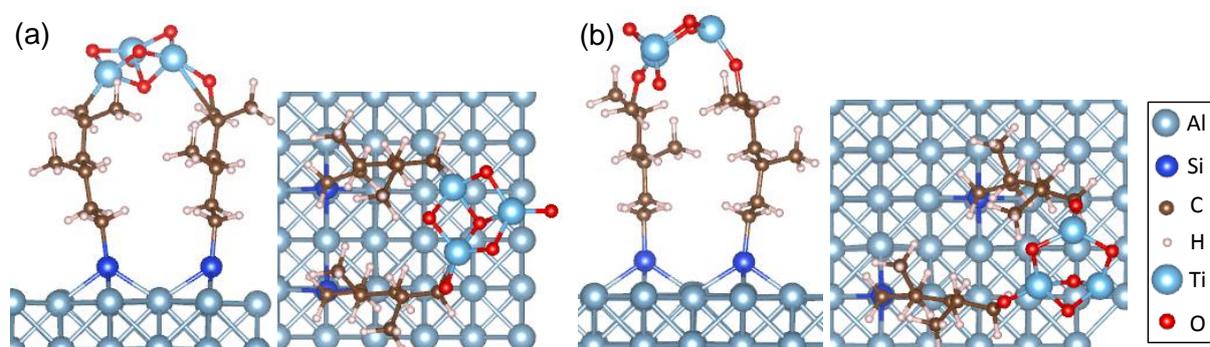
Figure 7: Relaxed structure of Al (100)-Si-PP-Ti3O6 from side view (left) and top view (right) (a) the minimum energy structure; (b) structure with larger Si-Si distance

Conclusions

To lay the foundation for the development of a new concept for the utilisation of metallised plastics as input for producing value-added components, we studied the structure of metallised plastics using experimental techniques and first principle calculations. Microstructure analysis, FTIR and LA-ICP-MS results of our sample showed that metallised plastics contain Al, as the metal part, and PP, as the polymer part, and Ti, in the pigment of colour. XPS data also showed the presence of C-Si bonds in the sample, due to the modification of the polymer layer to bind with the metal layer. We have also presented the density functional calculations of the PP deposited on the Al surface. We investigated the preferential deposition site for PP on Al (100) with a Si link. The binding energy of PP on Al (100) through Si binding was 3.79 eV, which is significant. Our charge transfer analysis showed that the charge transfer in PP deposited on the Al (100) surface with a Si link occurred from the polymer to the metal. We also investigated the interface between the polymer and the metal. The electronic structure suggests that the binding of Si with the Al surface decreases upon deposition of PP, while no significant modification in the Al surface is observed.

These results show fairly strong binding between the different elements in the structure of metallised plastics structure. Consequently, recycling each component separately would be a formidable task. To successfully recycle these materials, we must reimagine metallised plastics and consider them as a single component or input, and potentially good source of Al, C, Si and Ti. Extracting these elements as raw materials using conventional mining consumes significant energy. Utilizing metalized plastics as an alternative source of Al, C, Si and Ti promises to reduce energy usage and greenhouse gas emissions, and alleviate the negative environmental impacts of landfilling and resource depletion. Understanding the structure of metallised plastics lays the ground work for the development of a new method for reusing metallised plastics. The results reported here will enable us to develop a new high temperature processes for transformation of metallised plastic to value added materials in an in-situ process. This single step process will reform metallised plastic in its atomic level and produce an advanced metallic alloy component. This study promises to pave the way for utilizing waste metallised plastics as a raw material in manufacturing industries.

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