

Colorbond® meets nanotech: understanding coating interactions with the environment

Colorbond is an Australian icon and an export success story. What the TV commercials don't show is that the Colorbond coating is as complex as it is attractive. BlueScope Steel conducts a continual testing and development program for Colorbond, and over the last several years the company has supported theoretical studies of the material's performance at the nanoscale. Here, we highlight some of the recent developments.

What is Colorbond?

Colorbond is more than just a pre-painted steel product; it is a carefully designed multilayer system that offers corrosion protection, enhanced durability, improved flexibility and great looks, among other important properties. As detailed by BlueScope Steel, 'the secret is a four-stage process'¹ (Fig. 1):

1. A Zinalume® steel base ensures outstanding anti-corrosion performance.
2. A conversion layer is chemically applied to enhance coatings adhesion.
3. A primer is baked onto the surface.
4. A durable exterior top coat is baked on.

Fundamental understanding of nanoscale interactions between the layers has been crucial for design of the multilayered coating with improved properties. Recent developments in molecular simulation techniques for predicting the bulk and interfacial properties of materials of disparate nature enabled us to understand some of the Colorbond interlayer properties.^{2,3} Our most recent work^{4,5} has been concentrating on understanding the nanoscale properties of the top layer, which forms an interface with the

environment and provides the first line of defence against the elements.

Molecular models of Colorbond

A search for new and improved materials for coating systems requires a detailed understanding of the structure-property relationships of the components. Although some properties of coating systems can be obtained experimentally, an ability to predict properties of coatings prior to laboratory synthesis can significantly facilitate new coating design. Interlayer adhesion, barrier properties and durability are some of the most important material properties requiring understanding at the molecular level. To facilitate such an understanding, molecular models of the essential system components have been designed in full detail and careful simulations performed to reveal fundamental property trends.³

To enable a realistic nanoscale representation of a cured paint surface, we have developed a methodology for construction of atomistic models of cross-linked polymer networks.³ The simulations allowed the cross-link density and the amount of free cross-linking sites in the coatings to be predicted. Shrinkage of the resin upon curing was also reproduced by the simulation. The methodology has been applied to low molecular weight resins cross-linked with different curing agents that represent typical primer coatings on steel. The methodology developed has also been used to create a cross-linked

model of a polyester-based paint, typical of a high-performance top coat.

To understand interactions within the Colorbond system, atomistic models of interfaces between an inorganic substrate and primer as well as between the primer and the top coat have been constructed. Using the models, we have calculated adhesion strength and barrier properties of the materials while also revealing the fundamental trends and molecular mechanisms of the materials performance as a function of chemical composition.^{2,3}

In our most recent work, we have employed the molecular models to understand interactions between typical top coats and environmentally borne particles. Equipped with the fundamental knowledge, researchers in BlueScope Steel laboratories can tailor the materials for a variety of environmental conditions and applications.¹

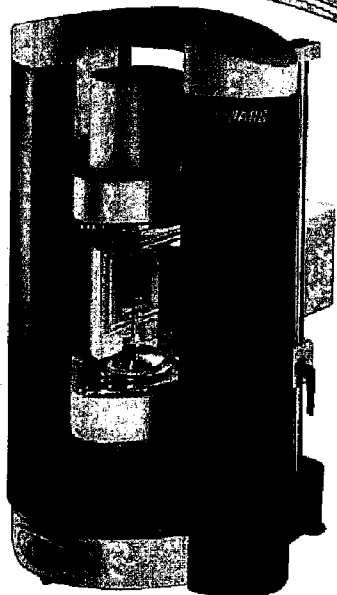
Understanding the environmental performance of the top coat

An important aspect of the top coat performance is its ability to withstand the harsh environmental conditions. Therefore, it is important to understand interactions between the top coat and environmentally borne particles. Many commercial paints are hydrophobic and tend to attract hydrophobic particles, such as carbonaceous solids^{6,7} arising from biomass and biofuel combustion.⁸

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Figure 1. (a) A Colorbond® roof. (b) The four-stage corrosion protection process.¹

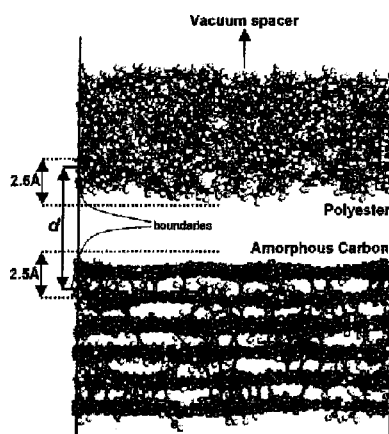


Figure 2. Schematic representation of polyester-amorphous carbon interface. Also included is the interfacial separation (d), defined as the distance between the surface boundaries of the two models.⁵

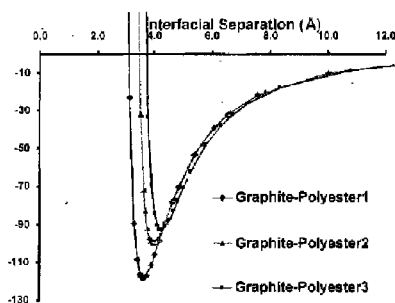


Figure 3. Sample adhesion curves for graphite-polyester interfaces showing the effects of nanoscale polyester surface treatments.

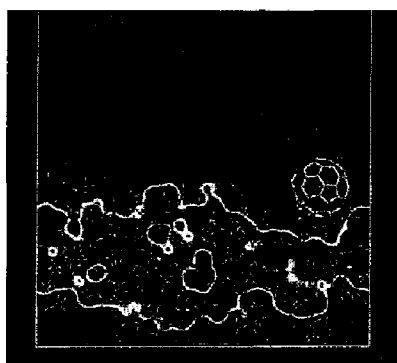


Figure 4. Slice of Van der Waals' surface, highlighting interaction of fullerene with polyester surface.

Depending on the nature of the fuel and the combustion conditions, the black carbonaceous residue can display a range of particle types with distinct properties including tar balls and soot. Tar balls have been identified by Pósfai et al.⁸ as amorphous carbonaceous spherules with diameters typically between 30 and 500 nm. In contrast, the primary particles of soot are spherical, with diameters of 20–30 nm, and comprise an onion-shell structure composed of approximately 7–10 graphite (0 0 1) planes, often surrounding an amorphous core.⁹ We have, therefore, recently used graphite as well as our novel amorphous carbon model¹⁰ and fullerenes to simulate Colorbond interactions with a variety of atmospheric carbonaceous particles in full atomistic detail.

A number of experimental studies have investigated procedures to modify the surface of organic polymer materials to either resist adhesion or alternatively to aid in adhesion to other surfaces. For example, Allman et al.⁶ reported on a commercial alkyl ammonium bromide finish for polyester, polyester/cotton and cotton fabrics that provided resistance to soiling. Similarly, Reeves et al.⁷ discussed a carboxymethyl cellulose finish that also offered improved resistance to soiling of polyester-based fabrics. In both examples, the improved resistance was believed to be due to the introduction of polar hydrophilic groups enabling hydrogen bonding with water. Other studies directed towards modifying the surfaces of hydrophobic polymers have involved atmospheric plasma treatment and oxidation with ozone and/or irradiation with ultraviolet light. It is therefore of interest to investigate in greater detail the molecular mechanisms of the effects of surface modifiers on polymer adhesion to carbonaceous particles.

Using classical molecular simulation techniques, we have been investigating interactions between polyester-based materials and graphite,^{4,5} amorphous carbon and neutral and charged fullerenes. An

example of a unit cell representing a periodic fully atomistic interface model is illustrated in Figure 2. We have tested both hydrophilic and hydrophobic nanoscale modifiers introduced onto the previously developed model polyester surfaces⁵ in order to determine the fundamental effects of such modifiers on the adhesion energetics between a range of paint surfaces and carbonaceous particles. Some of the adhesion calculation results are illustrated in Figure 3 and clearly show the effects of polyester surface modifications.

Adhesion energetics have been calculated using the COMPASS (Condensed-phase Optimized Molecular Potential for Atomistic Simulation Studies) forcefield¹¹ to describe interatomic interactions. COMPASS is an ab-initio force field with parameters derived from approximate solutions of the full Hartree Fock equations, and optimised for a wide range of condensed matter properties using experimental data. The parameterisation to condensed phase properties used in this forcefield is ideal for application to adhesive energy calculations between dense surfaces and has been demonstrated to produce reliable results for our systems of interest.^{4,5,11}

We have employed a number of computational procedures to investigate a variety of conditions and a range of the surface treatments, which may affect the adhesion of modified polyester systems to carbon-based materials. The conditions considered include forming a rigid interface by suppressing relaxation of the surfaces, undergoing molecular dynamics at

room temperature (298 K) to enable relaxation, and simulating conditions above the glass transition temperature of polyester-based systems by carrying out molecular dynamics at 400 K. Complete details of the simulation methodology can be found in previous publications.⁵

Our results indicate that van der Waals' interactions play a significant role in adhesion between the carbonaceous surfaces and polyester. For example, molecular dynamics simulations at 298 K showed that van der Waals' forces are sufficiently strong to cause physisorption of the neutral fullerene particle on to the polyester surfaces (Fig. 4). Based on our theoretical simulations we have suggested that increasing the hardness and atomic roughness of the polyester surface by cross-linking and/or carefully chosen nano-functionalisation can significantly decrease its interactions with the carbonaceous solids and nanoparticles.^{4,5} BlueScope Steel considers ways of achieving such surface properties, exploring a number of surface treatment and self-assembly techniques.

Acknowledgments

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