GCEP Progress Report for Advanced Transportation

Transportation Vehicle Light-Weighting with Polymeric Glazing and Mouldings

Investigators

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Abstract

Polymeric glazing and mouldings are an extremely high "want" from the transportation community, enabling more creative designs as well as improved part consolidation。 However, plastic windows and mouldings must have high-performance and low-cost protective coating systems with lifetimes in excess of 10 years. Current polymeric glazings do not meet durability/performance requirements for near-term implementation. Our project targets new coating system manufacturing to address durability and cost issues necessary to meet or exceed transportation engineering requirements.

Atmospheric plasma deposition (APD) is an emerging technique that enables plasma deposition of coatings on large and/or complex geometry substrates in ambient air without the need for expensive vacuum or inert manufacturing platforms. It is an environmentally friendly and solvent-free technique, minimizing chemical waste throughout the process as well as greenhouse gas emissions when compared to current wet chemistry aqueous sol-gel manufacturing techniques. Low deposition temperatures (<50°C) allows the deposition on plastic and organic substrates.

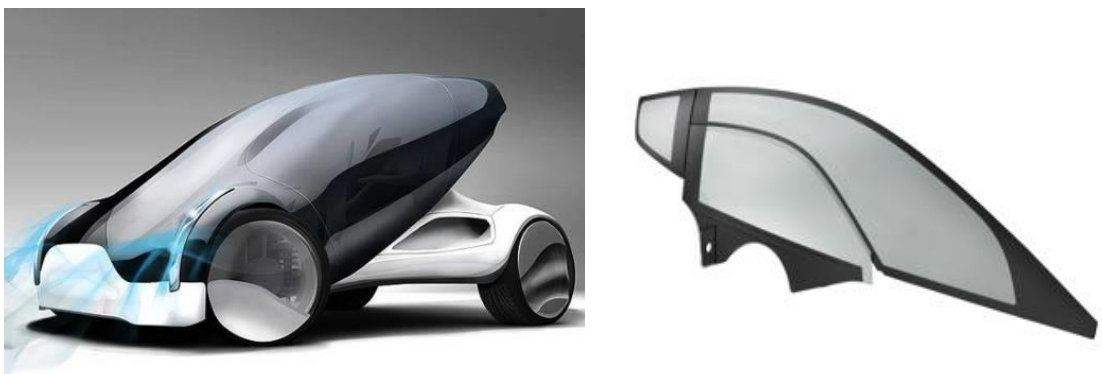
Using our state-of-the-art APD coating capabilities, we have demonstrated the ability to deposit highly transparent bilayer organosilicate coatings with superior combinations of elastic modulus and adhesion compared to commercial sol-gel coatings. The bilayer is deposited on large substrates by atmospheric plasma, in ambient air, at room temperature, in a one-step process, using a single inexpensive precursor. The significantly improved elastic modulus translates into improved durability and resistance to scratching and environmental degradation. The method overcomes the challenge of fabricating coatings with both high mechanical and interfacial properties in a one-step process – this would generally require at least a three-step process that includes a surface preparation step, and two coating operations. In APD, the surface is functionalized simultaneously as the first layer is deposited, thereby reducing the total number of processing steps. In this way, we can deposit a tough carbon-bridged hybrid silica layer with excellent adhesion to plastics followed by the deposition of a top layer formed of a dense silica with high elastic modulus, hardness and scratch resistance. The bilayer structure exhibited a remarkable ~100% visible transmittance, twice the adhesion energy and three times the elastic modulus of commercial polysiloxane sol-gel coatings currently in use today for aerospace applications.

For making these plasma deposited mechanically robust protective coating multifunctional, functional nanoparticles are successfully incorporated into these plasma deposited organosilicate matrix for making nanocomposites. Silica nanocomposites and ceria nanocomposites are demonstrated here as examples.

Introduction and Background

Polymeric glazing and mouldings are an extremely high "want" for the transportation community. They enable more creative design and improve part consolidation. Polymeric glazing and mouldings are inherently lightweight materials that may find exciting opportunities in the transportation industry as a means of increasing fuel efficiency. With 75% of fuel consumption relating directly to vehicle weight, potential weight reductions that result in an improved price-performance ratio promotes the use of lightweight materials [1]. Generally, polymeric glazing and mouldings can reduce weight by as much as 15 kgs per vehicle for glazing alone. Considering both the mature U.S. market and the emerging Chinese market, there is the potential for staggering reductions in vehicle weights, totalling 195 million kg and 450 million kg for the U.S. and China respectively. Globally, this figure sores above 1 billion kg in possible weight reduction.

One of the key plastics used in automotive sector is polycarbonate (PC). PC has dominated the market for vehicle headlamp covers for 15 years, and now it challenges glass in windows. Plastics are lightweight materials ideal to improve fuel efficiency and design flexibility without compromising on performance or safety. Polymeric moulding processes enable glazings to be formed into shapes that are not feasible with conventional glass forming processes. This technology is therefore seen as one of the key enablers for future design leadership and is currently unavailable due to performance shortcomings. **(Fig. 1)**



(a) (b)

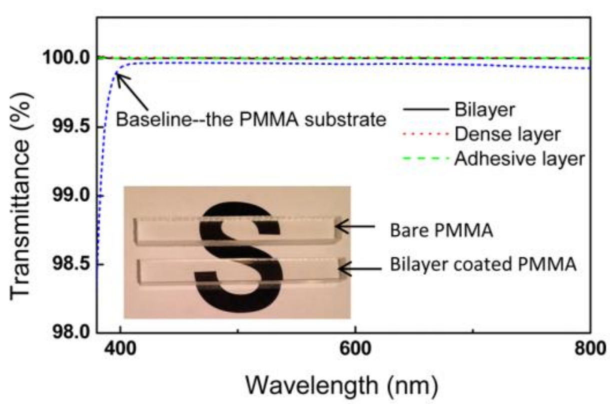
Fig.1: (a) The concept car designed and manufactured by polymeric glazing and mouldings, (b) The side window fabricated by PC on Volkswagen hybrid concept car XL1[1].

Transparent and high-performance coatings on plastic substrates offer the possibility of significant light-weighting and improved aerodynamic design for transportation vehicles. For example, weight reduction together with significant lowering of vehicle center-of-mass can be achieved by replacing automobile glass with plastic (poly-methyl methacrylate (PMMA), polycarbonate (PC) or polyvinyl) windows. Low-cost, light weight and recyclable reinforced organic mouldings can also be used to replace metallic mouldings and improve the aerodynamic design envelope. However, the use of plastic windows and mouldings must have high-performance and low-cost protective coating systems with lifetimes in excess of 10 years. Current polymeric glazings do not meet durability/performance requirements for near-term implementation. For example, current commercial sol-gel based polysiloxane coatings for plastic windows in commercial aerospace systems do not have the desired combination of low-cost processing, weather and scratch resistance, along with long-term durability in terrestrial environments. Our project will target new coating system manufacturing to address durability and cost issues necessary to meet or exceed transportation engineering requirements. An experimental approach based on fundamental chemistry exploits innovative deposition and coating technologies with detailed surface analytical measurements and targeted physical testing.

Atmospheric plasma deposition is an emerging technique that enables plasma deposition of coatings on large and/or complex geometry substrates in ambient air without the need for expensive vacuum or inert manufacturing platforms. It is an environmental friendly technique with the advantage of minimal chemical waste throughout the process and is solvent-free with the potential for zero greenhouse gas emissions compared to current wet chemistry aqueous sol-gel manufacturing techniques. Low deposition temperatures (<50°C) allows the deposition on plastic and organic substrates.

Results

Using our state-of-the-art atmospheric plasma deposition coating capabilities, we have recently demonstrated the ability to deposit highly transparent bilayer organosilicate coatings with superior combinations of Young's elastic modulus and adhesion compared to commercial sol-gel coatings **(Fig. 2)**. The bilayer is deposited on large substrates by atmospheric plasma, in ambient air, at room temperature, in a one-step process, using a single inexpensive precursor. The significantly improved Young's modulus translates into improved durability and resistance to scratching and environmental degradation. The method overcomes the challenge of fabricating coatings with both high mechanical and interfacial properties in a one-step process – this would generally require at least a three-step process that includes a surface preparation step, and two coating operations. Deposition of the bottom coating includes the ability to simultaneously functionalize the surface while depositing a tough carbon-bridged hybrid silica layer with excellent adhesion to plastics followed by the deposition of a top layer formed of a dense silica with high Young's modulus, hardness and scratch resistance. The bilayer structure exhibited a remarkable ~100% visible transmittance, twice the adhesion energy and three times the Young's modulus of commercial polysiloxane sol-gel coatings currently in use today for aerospace applications. [2]



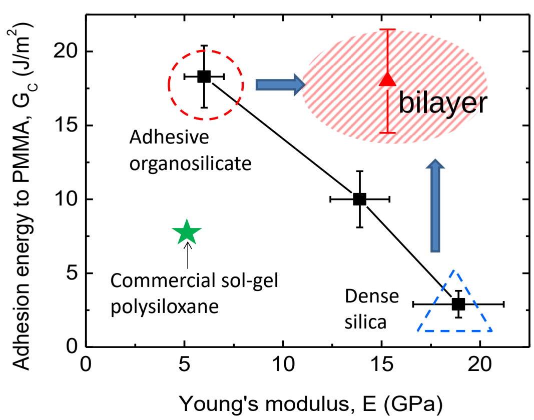
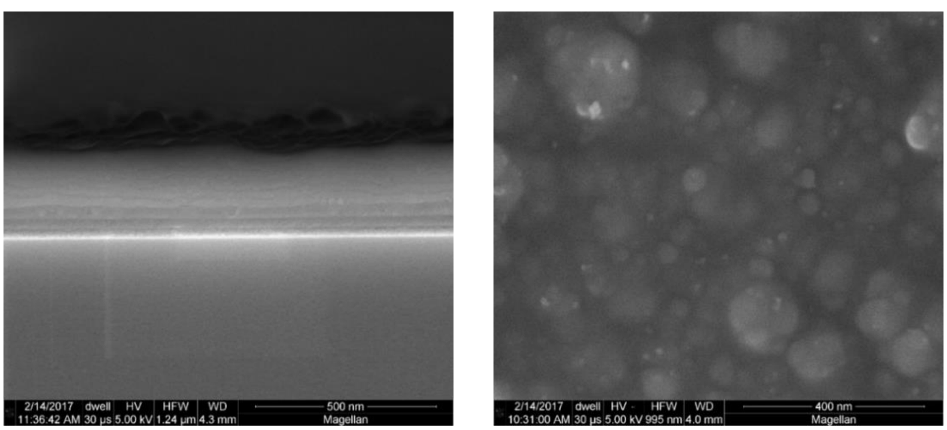


Fig. 2: High-performance and transparent bi-layer coating on PMMA deposited using atmospheric plasma has much better combination of Young's modulus (scratch resistance) and adhesion (durability) compared to commercial sol-gel polysiloxane coatings [2].

Incorporate UV Protection:
In an attempt to enhance the sustainability of plastics for advanced transportation systems, we promoted appropriate multifunctional properties to the thin films which will prevent damage of the surface from both scratches and UV radiation, while preserving the high transparency of the material. To address this issue, here we demonstrated two distinct strategies: 1. Incorporating nanoparticles into a host plasma deposited organosilicate matrix, and 2. direct deposition of UV-absorbing organosilicate coatings using dual precursor APD.

<u>1. Incorporating nanoparticles into a host plasma deposited organosilicate matrix</u>

The incorporation of nanoparticles such as metal oxides (e.g. TiO_2, ZrO_2, SiO_2) into the coating would protect the polymer substrate against mechanical and photo-degradation, while the plasma deposited matrix can still provide enhanced adhesion to the substrate, durability and resistance to scratching and environmental degradation. For nanocomposite deposition, we combined an ultrasonic spraying head with the atmospheric plasma system, co-depositing nanoparticle together with the matrix made with APD. Silica nanocomposite and Cerium oxide nanocomposite are demonstrated. For silica nanocomposite, functionalized silica nanoparticle dispersed in water with effective diameter less than 25nm were used. We found that having well dispersed nanoparticles are important for smooth surface morphology and optimized optical and mechanical properties. Figure 3(a) and 3(b) shows the SEM cross section and top-down view of the resulting nanocomposite film with ~20 wt% of silica nanoparticles incorporated. The thickness is around 350nm with relatively smooth surface and the nanoparticles are well dispersed in the matrix. The transmittance of the matrix, the nanocomposites with ~10wt%, ~20 wt%, and ~30 wt% silica nanoparticles were measured by UV-Vis. The matrix shows a ~100% transmittance in the visible range as expected. The composite films are also highly transparent in the visible range with a >99% transmittance for the 10wt% one, a >98% transmittance for the 20wt% one and a >95% transmittance for the 30wt% one. The hardnesses of the coatings were determined by the nano-indentation and show a peak average value (~75% enhancement comparing to the matrix) when 20wt% nanoparticle was incorporated. The enhancement of hardness indicates a strong interaction between the matrix and the nanoparticle as weak interfacial interaction cannot transfer load from matrix to the nanoparticle that will result in a weaker material. We believe the strong interfacial interaction comes from activation of the nanoparticle surface during plasma exposure.



(a) (b)

Fig.3 (a) Cross-section, (b) Top-down, SEM images of SiO_2 (20wt%) nanocomposites

We also incorporated CeO_2 nanoparticle for UV-protective purpose. For a ~550nm thick composites with ~20 wt% nanoparticle, a >90% transmittance in the visible range was achieved while absorbing ~50% of UV light. XPS depth profiling indicates that unlike a lot of solution based deposition techniques, no phase segregation throughout the thickness occurred during this deposition process. It ensures that no weak interface will form due to nanoparticle segregation at the interfaces.

2. Direct deposition of UV-absorbing organosilicate coatings using dual precursor APD.

The UV-absorbing organosilicate protective coating is also successfully deposited via a dual precursor atmospheric plasma deposition strategy with an UV-absorbing precursor, 1, 4-Bis(triethoxysilyl)benzene (BTESB), and a buffering precursor, toluene. Benzene and its oxidized derivatives are widely used UV-absorbing structure. The challenge of incorporating these UV-absorbing functional groups into the organosilicate protective coating comes from their instability in oxidative atmospheric plasma environment. They can be easily destroyed under the atmospheric plasma, losing their UV-absorbing ability. In this work, in order to protect benzene structure from fragmented by plasma, we utilized an effective buffering precursor, toluene, which preferentially react with plasma active species that causes benzene oxidation. FTIR spectra of coatings using single BTESB precursor with two different plasma conditions, and dual BTESB + toluene are collected. Stronger peaks at $1385cm^{-1}$ and $1430cm^{-1}$, which are attributed to benzene-Si structure, in dual precursor spectrum confirmed the preservation of more benzene ring when toluene is used. The resulting coatings deposited using dual precursor method showed better UV-absorbing and 70% enhancement on adhesion properties than single precursor counterparts. (Figure 4) The resulting film with dual precursor strategy showed effective UV-absorbing property, ~100% transparency in the visible light wavelength region, and ~5 times the adhesion energy to PMMA than commercial poly-siloxane sol-gel coatings.

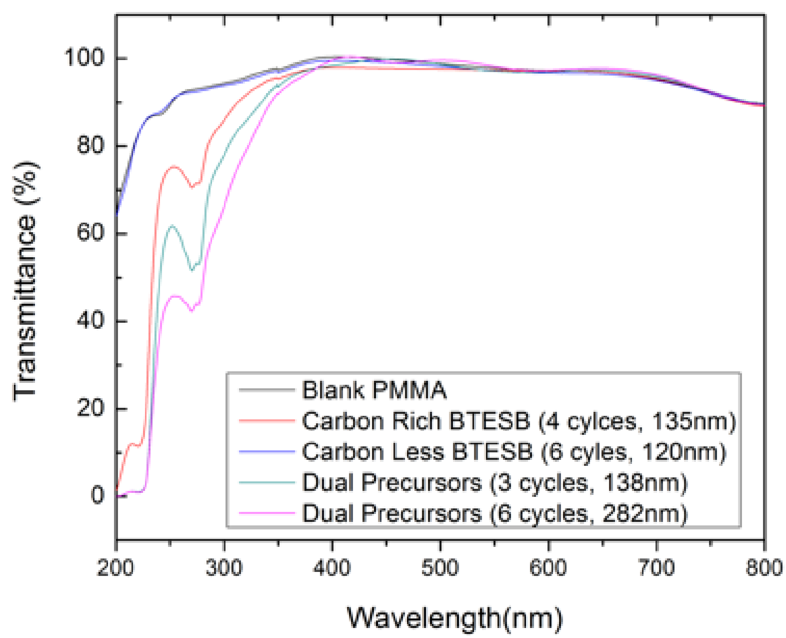
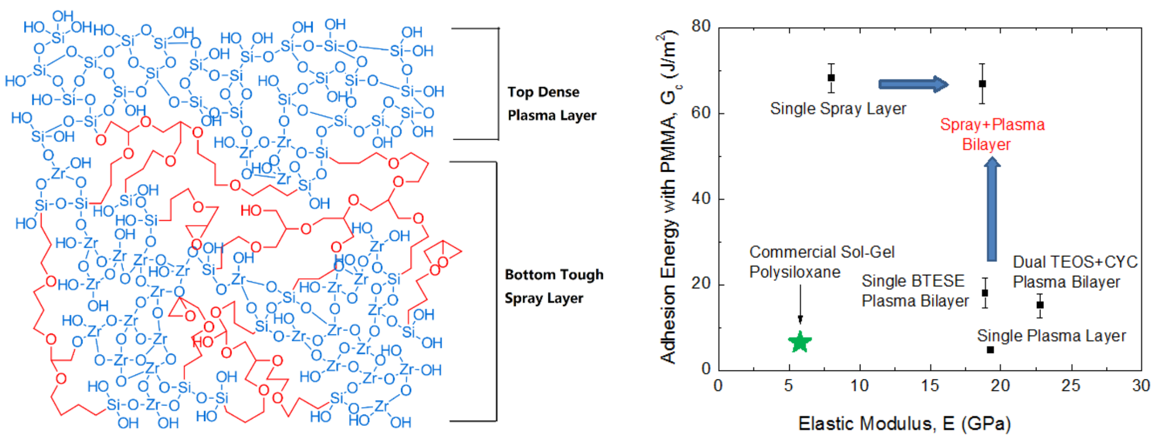


Fig. 4 Optical properties for organosilicate coatings deposited by BTESB as a single precursor with different deposition conditions and dual BTESB +toluene

Combining Plasma with Ultra High Adhesive Spray Coated Hybrid layer:

We have demonstrated APD as an effective way for depositing high performance protective coatings on plastics with both high hardness and adhesion. However, the deposition rate of APD is generally lower than conventional solution based sol-gel techniques. Other transparent silica protective coatings have been deposited using wet chemistry techniques before, but the interfacial adhesion with plastics is generally not determined or in the low range. In this study, we demonstrate the successful deposition of a highly adhesive inorganic-organic hybrid coating on plastics using (3-Glycidyloxypropyl) trimethoxysilane (GPTMS) and tetrapropyl zirconate (TPOZ) as precursors with spray coating deposition. The resulting film consists of an interpenetrated organic and inorganic molecular network as shown in Figure 5(a). By optimizing GPTMS/TPOZ ratio, an adhesion energy of more than 65 J/m^2 was achieved with delamination occurred cohesively within the PMMA substrate. Hard dense layer was successfully deposited on top of the hybrid adhesive layer by APD to create a bilayer structure. During deposition, APD was found to simultaneously activate the surface of the bottom adhesive layer by creating hydrophilic groups (-OH, C=O, etc), which ensures a strong bilayer interface. The resulting bilayer structure showed >90% transparency in the visible region, ~eight times the adhesion energy and four times the surface hardness of commercial poly-siloxane sol-gel coatings. The approach provides a strategy for unprecedented combination of adhesion and mechanical properties.



(a) (b)

Fig.5 (a) Schematics of the molecular structure of the bilayer coating and (b) its mechanical properties as compare to commercial sol-gel polysiloxane coatings and other coatings deposited by atmospheric plasma

Progress

In the past year, we focused on creating mechanically robust polymeric glazing that offers UV-protection to the underlying polymer substrate. We demonstrated two distinct strategies: 1. Incorporating nanoparticles into a host plasma deposited organosilicate matrix, and 2. direct deposition of UV-absorbing organosilicate coatings using dual precursor APD. The resulting films shows high transparency in the visible range but absorbing significant amount of UV light. The mechanical properties of these films are not compromised but even enhanced in terms of the hardness and adhesion. We also developed an ultra-high adhesive spray coated hybrid layer on PMMA which is compatible with the plasma deposited dense layers. By optimizing the sol-gel chemistry, an adhesion energy of more than 65 J/m^2 was achieved with delamination occurred cohesively within the PMMA substrate.

Future Plan

Mechanically robust multifunctional polymeric glazing:
With the ability to deposit nanocomposite using a combination of APD and ultrasonic spraying, we plan to create mechanically robust nanocomposite which offers other functionalities, such as: High electrical conductivity, Self-cleaning, IR-absorption and so on.

Process Diagnostics: we are currently bringing a new mass spectrometer detection tool online, which should greatly enhance our insight into atmospheric plasma chemistry. The possibility to use in-situ gas chromatography with mass spectrometry (GC-MS) detection to analyze exhaust gases can provide further insights into the deposition mechanisms as well as provide an efficient manner to carefully monitor the plasma process. This system will allow us to both evaluate precursor reactivity and aid in the identification and quantification of the most abundant stable by-products generated by plasma dissociation. It should then be possible to correlate the plasma chemistry with the chemical composition and structure of the elaborated coatings and to report the main plausible reaction pathways occurring during deposition. Beyond improving the understanding of the underlying fundamental aspects of atmospheric plasma chemistries, this capability should act as an effective tool to improve the properties of our coatings and push forward the performance of our materials.

Publications and Presentations

Publications

1. Yichuan Ding*, Siming Dong*, Jiahao Han, Dongjing He, Zhenlin Zhao and Reinhold H. Dauskardt, "Optical Transparent Protective Coating for Plastics", in review.

Presentations

1. Reinhold Dauskardt, "Atmospheric Plasma Deposition of Transparent and Conductive Films", invited presentation at the **43rd International Conference on Metallurgical Coatings and Thin Films**, San Diego, CA.

2. Yichuan Ding, Siming Dong, Dongjing He, Zhenlin Zhao, Reinhold Dauskardt, "Combining Spray and Atmospheric Plasma Deposition of Transparent Bilayer Protective Coatings on Plastics with Exceptional Adhesion and Hardness", **ACS 253rd National Meeting & Exhibition**, San Francisco, CA, April 2017.

3. Siming Dong, Yichuan Ding, Dongjing He, Zhenlin Zhao, Reinhold Dauskardt, "Dual Precursor Atmospheric Plasma Deposition of Organosilicate Transparent Functional Coating on Plastics", **ACS 253rd National Meeting & Exhibition**, San Francisco, CA, April 2017.

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1. Zbindendesign, August 25, 2014. Designing Glass for Style – polycarbonate, retrieved from https://zbindendesign.wordpress.com/2014/08/25/designing-glass-for-style-polycarbonates.
2. Linying Cui, Krystelle Lionti, Alpana N. Ranade, Kjersta Larson-Smith, Geraud Dubois, and Reinhold H. Dauskardt, "Highly Transparent Multi-Functional Bilayer Coatings on Polymers Using Low Temperature Atmospheric Plasma Deposition", **ACS Nano**, 2014. DOI: 10.1021/nn502161p.