Nanocomposite thin film coatings for brittle materials

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Abstract
The development of polymeric coatings for brittle substrates such as ceramics or glass is an important technological goal, the aim of which is to provide protection or enhance the mechanical properties of the substrate. In this work we propose a novel one-step approach, evaporation-driven self-assembly of polymers, to coat Al$_2$O$_3$ substrates with a thin nanocomposite coating. The films consist of polyvinyl butyrate polymer and either multi-walled carbon or tungsten disulfide nanotubes, which are found to improve both the strength and toughness of the brittle alumina substrates via crack bridging and crack propagation inhibition mechanisms.

Keywords EDSA, Multi-walled carbon nanotubes, Tungsten disulfide nanotubes, Three-point bending, Work of fracture, Brittle substrates

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Introduction
Polymer thin film coatings have significant technological importance due to their ability to modify the chemical, optical, thermal, electrical, and/or mechanical properties of a surface. Their practical applications span from making a conductive layer on an otherwise insulating substrate, to hermetically proofing moisture-sensitive materials, to chemically functionalizing an inert surface, to improving the mechanical performance of the coated interface.\textsuperscript{1-10} Such coatings can even be found in biogenic materials, such as turtle carapaces, where a thin keratin layer serves as an effective stress dissipater for a much thicker bony underlayer.\textsuperscript{11,12} Based on this example, a number of requirements can be proposed for adequate coatings: simplicity of the coating process, material economy, low thickness, good adhesion to the substrate and mechanical efficiency.

Prominent materials found in the current literature and industrial applications are carbon\textsuperscript{13} or inorganic\textsuperscript{14} nanotubes (CNT and INT, respectively). Due to their high aspect ratio, elastic modulus, and yielding stress,\textsuperscript{15-18} they are often used as additives in many polymer composites.\textsuperscript{19-26} However, their applications are limited only to small volume fractions (typically several percent or less), due to their poor dispersivity and a tendency to agglomerate.\textsuperscript{19,20,24}

Here we report a new processing approach for the coating of brittle substrates such as glasses or ceramics by means of a thin polymer–nanofiller composite film. While being approximately 1 volume % of the overall structure, the resulting film markedly improves the substrates’ flexural strength ($\sigma$) and fracture work ($W_f$). The coating technique is called evaporation-driven self-assembly of polymers, or EDSAP. The polymer used in this study is polyvinyl butyrate (PVB), and the nanofillers are multi-walled carbon nanotubes (MWNTs) and tungsten disulfide inorganic nanotubes (WS$_2$-INT).

Evaporation-driven self-assembly (EDSA) is a well-known technique\textsuperscript{27-30} for deposition of a thin layer of nanoparticles (and, specifically, nanotubes) on a vertical surface. It is based on a spontaneous process that occurs to a particle dispersion in a solvent upon evaporation of the liquid medium, and is commonly known as "coffee-ring effect."\textsuperscript{31} This process results from the complex balance between the liquid surface tension, the friction force of the contact line and liquid evaporation. The simplest example often described in the literature is that of a single drop of liquid with dispersed particles ("coffee droplet") on a flat surface:\textsuperscript{32,33} when a drop of coffee is left on a solid surface to evaporate, it leaves a dense agglomeration of coffee particles located mostly at the periphery of the droplet. When the droplet is drying, evaporation (which is assumed to be constant under stable conditions) reduces the height of the droplet at all points on the droplet surface. For an ideally smooth surface, the contact line is free to move and the droplet shrinks. Its spherical shape and contact angle remain constant, due to the surface tension (Fig. 1a). However, if this process takes place on non-ideal surfaces the contact line is often pinned to surface defects and the droplet is unable to shrink to compensate for the liquid loss: compensation is
done by a flow of liquid from the center of the droplet to the periphery, called Deegan flow\(^1\) (Fig. 1b). As the liquid flows from inside the droplet, it carries suspended particles or nanotubes. When the contact line is no longer pinned, and the droplet continues to shrink, the particles at the droplet periphery remain attached to the surface, forming a thin film. Evaporation continues as long as there is available liquid, resulting in a continuous film deposition.

According to the literature\(^{33}\) this droplet model can be applied to the case of a flat substrate standing vertically in an evaporating liquid (Fig. 1c). The function of the droplet contact line in this case is transferred to the meniscus contact line. The EDSA coating mechanism therefore results from a Deegan flow of particles inside the liquid toward the meniscus contact line and from particle attachment to the surface, as the meniscus recedes.\(^{30}\)

The EDSAP approach proposed here differs from that described above by the presence of low concentrations of soluble polymers (\(C_{\text{disp}}\)) in the evaporating liquid. Polymer chain molecules behave in a way similar to the dispersed particles and follow the Deegan flow toward the meniscus contact line. The result is a one-step procedure for preparation of a polymer film impregnated with particles, in this case, carbon or inorganic nanotubes. The film thickness and the concentration of nanotubes in the film are controlled by the polymer and nanotube concentrations in the initial dispersion. The insets on Fig. 1c show (from top to bottom) a pure PVB coating, a WS\(_2\)–PVB coating and an MWNT–PVB coating, respectively.

The resulting film is a nanocomposite coating with a high concentration of nanofiller reinforcements. The mechanical performance of the nanocomposite coatings was compared to that of pure polymer coatings and to that of uncoated substrate by means of a 3-point bending test. Fractured specimens were examined by electron microscopy.

**Materials and methods**

**Film preparation**

**MWNT–PVB films**

In a typical procedure CVD-grown MWNTs (50 mg, 0.5 mg/ml) were put into 100 ml of Tetrahydrofuran (THF) and sonicated for 20 min. Then, 1 ml of Tryton-X surfactant (1 wt%) and 0.5 gr of PVB (0.5 wt%) were added to the dispersion, which was sonicated for a further 2 h. The resulting dispersion remained stable for several weeks under ambient conditions. Al\(_2\)O\(_3\) (99.6% pure, as-fired, unpolished, purchased from Valley Design Corp., Shirley, MA), 0.25 mm in thickness, was cut using a diamond saw to 30 mm × 5 mm substrate slides. The slides were sonicated in DI water, ethanol, and acetone and then inserted into a specially designed EDSAP tank. The MWNT–PVB dispersion was filtered through cotton wool to remove large aggregates, and then added to the tank until the substrates were completely covered by the liquid. The tanks were left for 20 h under ambient conditions until all the solvent evaporated. The substrates were then carefully rinsed with water and dried under an air stream.\(^{30,35}\)

**WS\(_2\)–PVB films**

The same general procedure was used to prepare WS\(_2\)-INT films. 500 mg of WS\(_2\)-INT (5 mg/ml) powder was put into 100 ml of ethanol and sonicated for 20 min. Then, 1 ml of Tryton-X surfactant (1 wt%) and 1 gr of PVB (1 wt%) were added to the dispersion, which was sonicated for a further 2 h. The resulting dispersion remained stable for several weeks under ambient conditions, and then its color changed from dark brown to light brown due to WS\(_2\) nanotubes oxidation. The 30 mm × 5 mm × 0.25 mm Al\(_2\)O\(_3\) substrates were sonicated in DI water, ethanol, and acetone, then inserted into a specially designed EDSAP tank. The WS\(_2\)–PVB dispersion was then added to the tank until the substrates were completely covered by the liquid. The tanks were left for 30 h under ambient conditions until all the solvent evaporated. The substrates were then carefully rinsed with water and dried under an air stream.

**Pure PVB films (control)**

PVB films were prepared for control purposes. For that, 1 ml of Tryton-X surfactant and 1 gr of PVB were added to 100 ml of THF, which was sonicated for 2 h. The 30 mm × 5 mm × 0.25 mm Al\(_2\)O\(_3\) substrates were sonicated in DI water, ethanol, and acetone and then inserted into a specially designed EDSAP tank.
tank. The PVB solution was then added to the tank until the substrates were completely covered by the liquid. The tanks were left for 20 h under ambient conditions until all the solvent evaporated. The substrates were then carefully rinsed with water and dried under an air stream.

**Pure substrates (control)**

Uncoated alumina substrates were prepared for control purposes. The 30 mm × 5 mm × 0.25 mm Al₂O₃ substrates were sonicated in DI water, ethanol, and acetone and used without further purification.

**Bending tests**

Bending tests were performed in a 3-point bend configuration on a Bose ElectroForce 3200 UTM instrument, using two different cross head speeds. Half of the specimens were tested at a cross head speed of 3 μm/s (“slow fracture”), while the other half were tested at 3 m/s, to simulate impact (“fast fracture”). All specimens were pre-loaded at 0.5 N prior to fracture. At least ten specimens of each type were tested at each cross head speed.

Flexural strength (σ) and apparent work of fracture (Wf) at both “slow” and “fast” cross head speeds were calculated from the load–displacement plots. Strength was obtained as follows:

\[
\sigma = \frac{3F_{\text{max}}L}{2bh^2}
\]

where \( L \) is the support span, \( b \) is the specimen width, \( h \) is the specimen height, and \( F_{\text{max}} \) is the maximum force.\(^ {35,36} \)

The apparent work of fracture was calculated as follows:

\[
W_f = S_{\text{AUC}}/2bh
\]

where \( S_{\text{AUC}} \) is the total area under the load–deflection curve.\(^ {35,37,38} \)

The term “apparent” is used to emphasize that the apparent cross section (\( b \times h \)) is used to normalize the energy, rather than the true (and possibly tortuous) cross section.

**SEM analysis**

High-resolution scanning electron microscopy (HRSEM) pictures were taken with SUPRA-55 VP Zeiss and ULTRA-55 Zeiss (Oberkochen, Germany) microscopes using an In-Lens detector. Images were collected at an acceleration voltage of 3 kV and working distance of 4–5 mm. To prevent charging, the samples were sputtered with gold–palladium alloy prior to SEM imaging, using an Edwards (Sanborn, NY) S150 sputter coater.

**TGA analysis**

TA Q-series SDT Q600 Thermal Gravimetric Analyzer was used in all TGA measurements. Alumina crucibles were used. All measurements were performed in air atmosphere.

![Figure 2](image)

**Figure 2** Thermal and surface properties of the EDSAP nanocomposite films. a–c TGA analysis of the pure PVB, WS₂-PVB, and MWNT-PVB films, respectively (black lines). Grey lines on images b and c represent the TGA analysis of pure WS₂-INT and MWNT. The red ellipses show the nanotubes decomposition on the nanocomposite films thermograms. d–f SEM top-view images of the pure PVB, WS₂-PVB and MWNT-PVB films, respectively

**Table 1** Mechanical properties of uncoated and coated Al₂O₃ substrates

|                 | “Slow fracture” – 3 μm/s | “Fast fracture” – 3 m/s |
|-----------------|-------------------------|------------------------|
|                 | Strength, MPa | Work of fracture, kJ/m² | Strength, MPa | Work of fracture, kJ/m² |
| Al₂O₃ neat      | 342 ± 60     | 0.22 ± 0.05            | 409 ± 79     | 0.81 ± 0.11            |
| Al₂O₃/PVB       | 370 ± 49     | 0.27 ± 0.06            | 460 ± 60     | 1.11 ± 0.26            |
| Al₂O₃/PVB+WS₂-INT | 378 ± 68    | 0.32 ± 0.06            | 577 ± 85     | 1.27 ± 0.25            |
| Al₂O₃/PVB+MWNT  | 409 ± 43     | 0.31 ± 0.04            | 606 ± 112    | 1.24 ± 0.24            |
Figure 3  Fracture surfaces of the pure PVB, WS$_2$-PVB and MWNT-PVB nanocomposite films, respectively

Figure 4  SEM images of the reinforcement mechanisms found in WS$_2$-PVB nanocomposite films. a A crack in the nanocomposite film. b and c Zoom-ins of the Fig. a, showing WS$_2$ nanotubes inhibiting crack propagation. d WS$_2$ nanotubes pull-out from the crack edge. e WS$_2$ nanotubes bridging the crack in the Al$_2$O$_3$ substrate
It is important to note that although the concentration of nanotubes in the initial dispersion \( (C_{\text{disp}})^{\text{NT}} \) is low, the concentration of nanotubes in the resulting film \( (C_{\text{film}})^{\text{NT}} \) is unusually high. The reason is that whereas the amount of nanotubes is low relative to the volume of the solvent \( (C_{\text{disp}})^{\text{NT}} \), it is significantly higher relative to the amount of polymer in the dispersion \( (C_{\text{film}})^{\text{NT}} \sim (C_{\text{disp}})^{\text{NT}} / (C_{\text{disp}})^{\text{p}} \gg (C_{\text{disp}})^{\text{NT}}) \).

SEM images of the nanocomposite coatings show that the nanotubes typically remain in the plane of the coating, although some, especially shorter WS\(_2\) nanotubes, are arranged perpendicular to the polymer film (Fig. 2d–f). The roughness of the films is summarized in Table S1 in the Supporting Information.

The mechanical properties of uncoated and coated substrates, measured by both “slow” and “fast” 3-point bending tests are summarized in Table 1. In both cases, the difference between uncoated Al\(_2\)O\(_3\) substrates and PVB-coated substrates are less than 15%. However, in all cases, the nanocomposite coatings contribute significantly to both composite yield strength and work of fracture, as can clearly be seen from comparison between uncoated Al\(_2\)O\(_3\) substrates and PVB+nanofiller-coated substrates. Best results are achieved with MWNT–PVB coatings in a “fast” fracture experiment,

**Figure 5** SEM images of the reinforcement mechanisms found in MWNT-PVB nanocomposite films. a and b Top-view SEM images of MWNT pull-out. c and d Top-view SEM images of MWNT bridging a developing crack in the film (white arrows)
The fracture process of brittle materials is primarily governed by the evolution of pre-existing defects.\cite{25,26} It is proposed here that the reinforcement mechanism is through the inhibition of defects by bridging of small cracks within the polymer film and by the arresting of any further propagation.\cite{41,42} For nanocomposite films, in addition to strength enhancement due to the presence of nanotubes, an additional reinforcing mechanism is indeed revealed by the electron microscopy observations, namely crack bridging. Figure 3 shows fracture surfaces of PVB, WS$_2$–PVB, and MWNT–PVB coatings. In case of the latter two, the pulled-out nanotubes as a result of bridging are clearly seen. In addition, we managed to observe several cases where the Al$_2$O$_3$ substrate is fractured, but the nanocomposite film is not, and bridging by WS$_2$–INT can be observed almost in situ (Fig. 4c).

Figure 3b and c shows a number of voids and holes in the polymer layers. The majority of those voids stems from the nanotubes being pulled out of the polymer upon fracture. Note that the pure PVB coating has no visible voids. However, it is possible that some of the larger voids are defects that are created during solvent evaporation. This may potentially lower the film reinforcement and create a higher film variability.

Figure 4 shows several top-view images of WS$_2$ nanotubes that prevent cracks from growing further (Fig. 4a and its zoom-ins, b and c). The crack in Fig. 4a does not progress in a sharp, brittle fashion, but rather is blunt and “stitched” by the nanotubes present. Figure 4d shows WS$_2$ nanotubes pull-out from a face of such a crack. Figure 4e shows PVB surface through a crack in the Al$_2$O$_3$ with several WS$_2$ nanotubes bridging the crack (pointed to by yellow arrows). Figure S2 in the Supporting Information shows additional images of a fractured WS$_2$–PVB nanocomposite film with several prominent examples of nanotube pull-out. Figure 5 shows a top-view of carbon nanotubes pull-out (Fig. 5a and b) and crack bridging (Fig. 5c and d) in an MWNT–PVB nanocomposite film.

Based on the observations above, the proposed mechanism for the increase in strength and toughness of the substrates coated with a pure PVB film is a so-called “adhesive tape effect” observed previously in both biogenic and synthetic materials.\cite{35} This effect is significantly enhanced by addition of nanofillers into the polymer film. The nanofillers provide additional reinforcing mechanisms such as crack bridging, nanotube pull-out and, possibly, others (slowing down of crack propagation by nanotubes due to crack deflections). The difference between WS$_2$–INT and MWNT-reinforced specimen may be attributed to a different nanotube aspect ratio, which is significantly higher for carbon nanotubes.

To confirm our proposition we performed a Weibull statistical analysis on the results obtained by both “slow” and “fast” 3-point bending experiments. The results are summarized in Table 2. In all cases, the Weibull scale parameter (α) corresponds well with the measured yield strength of the substrates. In most cases the Weibull shape parameter (β), which reflects strength variability (higher values of β indicate lower variability), is larger for the coated substrates, which hints to the lower amount of critical defects or “defect nullification,” in good accordance with the SEM observations.

### Conclusions

A new, one-step procedure for nanocomposite coating of brittle substrates, called EDSAP was proposed. The procedure is based on an EDSA process and does not require special equipment or instrumentation. Resulting coatings contain high amounts of nanotube fillers, most of which are aligned in the plane of the substrate. The coatings are shown to improve the yield strength and work of fracture of alumina substrates by 19 and 40% respectively in a “slow” fracture process, and by 48 and 53% respectively in a “fast,” “impact-like” process. The overall volume fraction of the coating was found to be 1.6–2 vol%, and the weight fraction of the nanofillers in the coatings was 7 ± 2 wt% in case of MWNT, and 11 ± 2 wt% in case of WS$_2$–INT.

Simultaneous strength and toughness improvements exhibited by the coated specimens, are attributed to crack propagation inhibition, crack bridging, and nanotube pull-out,\cite{39,40} which are clearly visible in SEM observations.

It is important to note, that the materials used in the process are not limited to MWNT, WS$_2$–INT, and polyvinyl butyrate. Many combinations of polymers and nanofillers are possible, which opens exciting prospects for multifunctional coatings. For example, conductive polymers with carbon nanotubes may lead to new, mechanically stabilizing, conductive coatings for ceramics and glasses. In addition, increasing the nanotube concentration in the film, as well as the film thickness, may improve the mechanical performance of the coated substrates even further.

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### Disclosure statement

No potential conflict of interest was reported by the authors.

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### Table 2: Weibull scale (α) and shape (β) parameters of uncoated and coated Al$_2$O$_3$ substrates

| Coating                  | “Slow fracture” – 3 μm/s | “Fast fracture” – 3 m/s |
|--------------------------|--------------------------|-------------------------|
|                          | α, MPa | β | α, MPa | β |
| Al$_2$O$_3$ neat         | 371    | 5.7 | 444 | 4.9 |
| Al$_2$O$_3$/PVB          | 395    | 6.7 | 490 | 6.8 |
| Al$_2$O$_3$/PVB+WS$_2$–INT | 412 | 4.7 | 619 | 6.2 |
| Al$_2$O$_3$/PVB+MWNT     | 431    | 8.7 | 660 | 4.8 |

Where the nanocomposite coating of 2.5 μm increases the yield strength of the substrate by 48%, and the work of fracture by 53%. The large error bars in all measurements reflect the brittleness of the substrates.
to improved nanocomposites.” In addition, we acknowledge support from the G.M.J. Schmidt Minerva Centre of Supramolecular Architectures and the generosity of the Harold Perlman family.

**Supplementary material**

Supplemental material for this article can be accessed [here](http://dx.doi.org/10.2080/20503024.2016.1254926).

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