Hybrid Processing Method for Fabrication of 3D Layered Nanocomposite Materials

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ABSTRACT

Southwest Research Institute and Exothermics Inc. have been developing a hybrid processing method to fabricate macroscaled, layered nanocomposite materials that mimic the structure of nacre. Current research in the biomimetic field is pointing towards importance of two governing mechanisms that contribute towards energy dissipation in nacre: 1) platelet interlocking features and 2) strong adhesion of a ductile organic phase to the mineral plates. In our current study, we employed a vacuum roll coating process to prepare nano-engineered alumina inorganic platelets with precisely controlled size, shape and morphology of designed interlocking features through top-down physical vapor deposition of multilayer films on embossed substrates. Then a novel plasma source was employed in a roll-to-roll, layer-by-layer method to surface functionalize alumina platelets in order to modify interfacial strength with an organic matrix. Subsequently, slip casting was utilized to fabricate macroscale layered materials with desired in-plane alignment of platelets, physical packing characteristics and percolation behavior when compounded. The microstructure of all compositions of the fabricated nacre-like materials was examined using scanning electron and optical microscopy, while the mechanical properties were analyzed using three-point bend tests. In this presentation, an overview of hybrid processing method and resulting materials will be given with a specific focus on vacuum roll coating, plasma processing and surface functionalization.

Keywords: nanocomposite, platelets, plasma, nacre, slipcasting

1 BACKGROUND

The unique hierarchical structure and extraordinary mechanical response of nacre have influenced various approaches to develop synthetic hybrid inorganic-organic materials that mimic nacre. Current research in the field is pointing towards importance of other governing mechanism active in nacre beyond the highly organized microarchitecture. Among the various different mechanisms proposed in literature to contribute towards energy dissipation in nacre are 1) strong adhesion of a ductile organic phase to the mineral plates and 2) platelet interlocking features. Modeling studies have suggested organic interlayer adherence to platelets play a key role in toughening of nacre. Other studies also shown that interlocking features function as physical obstacles to relative movement of platelets that contribute to crack branching and blunting [1].

2 APPROACH

A aim of this effort was the execution of a design of experiments in which multi-variable processes that affect structure from molecular to macro-scale levels were examined towards demonstration and understanding of the structure-property relationships of layered materials. Figure 1 illustrates the technologies and cyle of development.

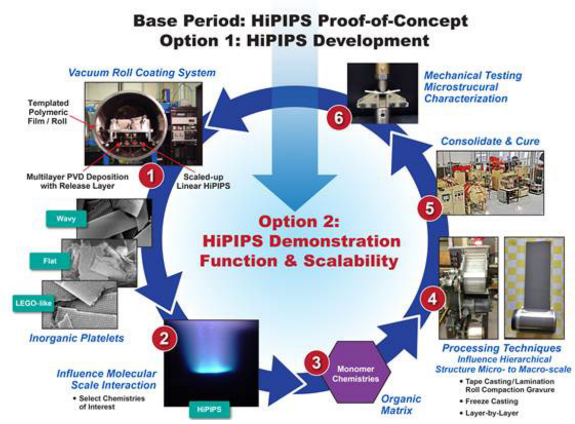

Figure 1. Schematic of Technology Pathway and Test Bed Cycle.

SwRI created a design matrix for the factors to investigate including possible combination levels for each input factor. A vacuum roll coating process was employed to reproducibly prepare appreciable quantities of inorganic platelets with precisely controlled stoichiometry, morphology and size through top-down physical vapor deposition of multilayer films on embossed substrates. For surface functionalization, high power impulse plasma source (HiPIPS), a new chemical vapor deposition technology that combines variable pressure plasma jets with advanced pulsed power technology was utilized. HiPIPS was utilized to apply Hexamethyldisiloxane (HMDSO) and Vinylphosphonic Acid Dimethyl Ester (VPA-DME) on a roll-to-roll process. Exothermics developed slip-casting and die-pressing processing methods to prepare macroscale samples. A custom fixture for 3-point bend testing was constructed and utilized to evalute layered composite samples.

3 RESULTS

The program was an integrated approach to fabricating a complex composite material possessing a hierarchical structure with dimensional lengths that span many orders of magnitude. The development of nanoengineered platelets, platelet surface functionalization, multi-layer composites and testing/characterization were running concurrently.

3.1 Nanoengineered Platelets

Vacuum deposition of a thin film onto a substrate and the subsequent comminuting of the film into a flake or platelet was originally developed for pigments that possess unique optical attributes [2]. Multilayer films deposited on release layers can be removed from the substrate to form free-standing planar platelets with very high aspect ratios. Roll-to-roll technology is available on the commercial scale that uses embossing and photocuring on a continuously moving plastic substrate to mass produce structured line resolutions of 1μm. The same process has been used to produce monosized particles of multi-micron width on microembossed plastic substrates from which they can be detached. Embossed substrates to make flakes of hexagon flat, hexagon wavy, and hexagon LEGO were originated with the resulting surface topography shown in Figure 2.

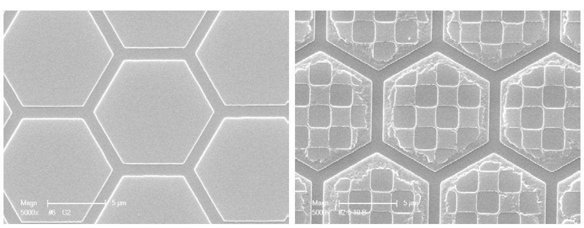

Figure 2. Hexagon flat and LEGO substrates.

When theses substrates were coated with alumina the resulting released platelets are shown in Figure 3.

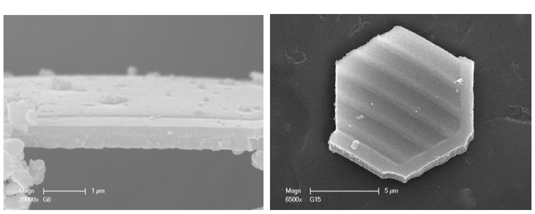

Figure 3. Hexagon flat and wavy platelets.

Utilizing vacuum roll coating, appreciable quantities of nano-engineered platelets were manufactured and sent to Exothermics for processing.

3.2 Platelet Surface Functionalization

High power impulse plasma source (HiPIPS), first reported under DARPA LoCo program in 2012, is a new chemical vapor deposition technology that combines variable pressure plasma jets with advanced pulsed power technology. In contrast to conventional state-of-the-art non-thermal atmospheric pressure plasma jets (APPJ) typically driven by RF or AC, the power densities and currents during pulse on-time are 2-3 orders of magnitude higher in HiPIPS. Since plasma is created through inelastic electron collision with precursor gas molecules, the increased power and current directly equates to significantly improved ionization and dissociation of precursor gases in HiPIPS.

For a precursor such as HMDSO, the use of HiPIPS results in the ability to control fragmentation of the precursor as shown in Figure 4. This control can then be tuned to result in optimization of the subsequent surface functionality.

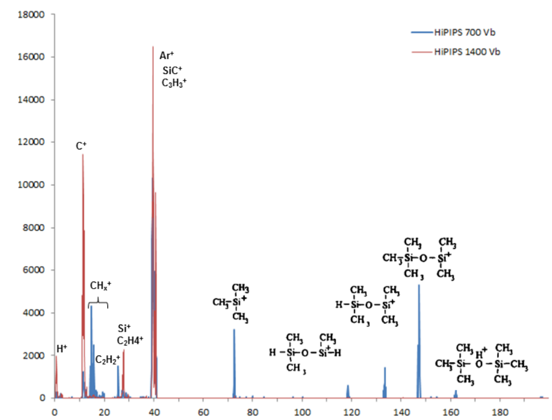

Figure 4. SIMS spectrum for HMDSO HiPIPS plasma operated at 700 and 1400V.

Two chemistries of interest were selected. HMDSO was selected for silicatization of the platelets. Silicatization of metal and metal oxides promotes the bonding to an organic matrix or resin. Dynamic deposition experiments were conducted on silicon wafer, stainless steel and alumina/sodium chloride coated PET substrates that mock roll to roll process in order to obtain thin film samples for SEM, FTIR, Raman, XPS and Auger analysis. XPS spectra corroborate FTIR and Raman analysis that demonstrate the presence of Si-C bonding in the thin films. Altogether, the results indicate successful silicatization using HiPIPS

VPA represents a unique class of chemical precursors for functionalization of inorganic particles or surfaces and subsequent formation of organic linkages via the reactive vinyl moiety. VPADME was chosen due to its high vapor pressure for easier use in plasma-based functionalization. XPS and Auger results confirmed Si, P, and O in films and lack of any metal contaminants. XPS C and P spectra corroborate FTIR and Raman analysis that demonstrate the presence of vinyl moeties and P-O bonding in the thin films. Altogether, the results indicate successful VPA-DME functionalization using HiPIPS

The scalability of HiPIPS was demonstrated with a 12 inch linear source on a roll-to-roll process shwon in Figure 5.

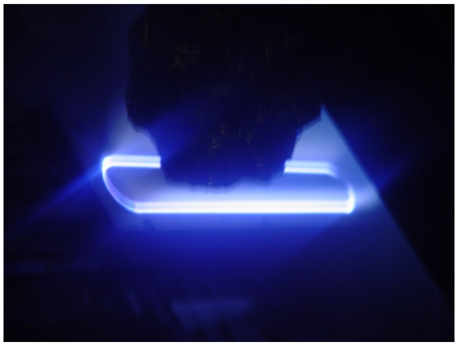

Figure 5. 12 inch linear HiPIPS source.

Following coating of the patterned substrate but prior to comminuting into platelets, 1000 feet of HiPIPS HMDSO plasma treatment and 500 feet of HiPIPS VPA-DME plasma treatment were functionalized. Additionally, the 500 ft of HiPIPS VPA-DME process was performed continuously for 13 hours with no issues in plasma or process instability. Additionally, quality assurance of HiPIPS treatment wasevaluated by performing FTIR analysis of communited platelets from different lengths along the 500 ft.

3.3 Multi-layer composites

Exothermics developed a slip-casting, hot isostatic pressing (HIP) processing method. An image of the Alumina slip-cast is shown in Figure 6.

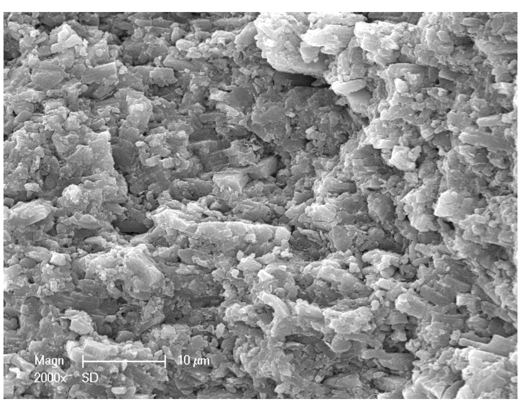

Figure 6. Hexagonal flat slip-cast.

It was identified that post-heat processing would adversely affect HiPIPS surface functionalization treatments. Exothermics investigated cold isostatic or die pressing techniques. Exothermics conducted investigations for development of slip-casting and die-pressing processing method to prepare macroscale samples. An image of the die press sample is shown in Figure 6.

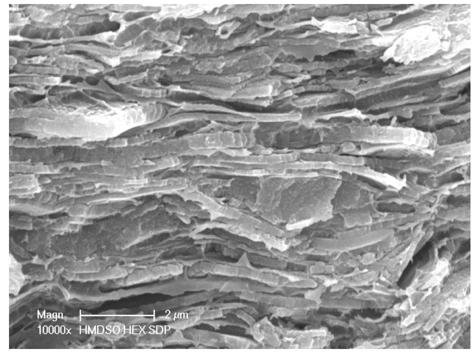

Figure 6. Die pressed hexagonal flat.

Initial slip cast, die-press sample were successful in that the samples had enough integrity and form to be handled as a macrosample. Yet, the uninfused samples could not be machined as the platelet layers are not sintered and fused together and thus shatter upon cutting. Infused samples are currently being evaluated for testing. Exothermics provided slip-cast samples, uninfused and PMMA-infused commercial platelets, for characterization and mechanical testing. Exothermics also investigated doctor blade trials using commercial platelets for process development.

3.4 Mechanical Testing and Characterization

3-point bend test suggest HiPIPS HMDSO and VPADME surface treatment of platelets to tailor interfacial properties improved mechanical properties. HiPIPS VPADME treated samples exhibit 100% increase in strength and toughness as compared to untreated samples.

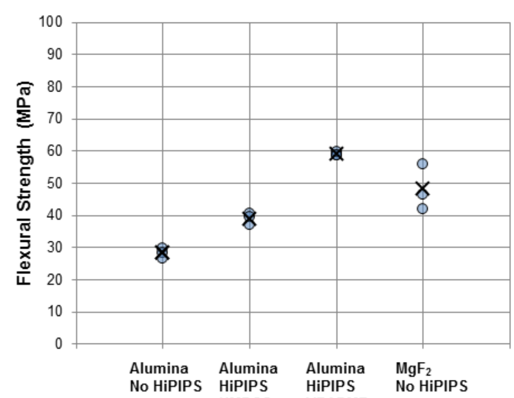

Figure 8. Mechanical testing- 3 point bend results.

4 DISCUSSION

The overall objective was to develop a large scale, thin film and surface treatment process using a novel high power impulse plasma source (HiPIPS) that would promote interfacial adhesion and thus improve mechanical properties of layered composite materials. The specific aims for were:

- Demonstration of scalability of HiPIPS through application to a 1 foot wide roll-to-roll process.
- Investigation of function of HiPIPS to dissociate molecular gas precursors for surface modification processes.
- Development and execution of an experimental design for a multi-dimensional layered composite materials test bed that examines effects molecular through macro-scale mechanisms on resulting structure-property relationship.
- Demonstration of HiPIPS ability to tailor surface interfacial chemistry for improved properties through investigation in a multi-dimensional test bed for manufacture of layered composite materials Identified issues with platelet manufacture and layered composite processing that are currently preventing full execution of DOE.

At the conclusion of the project the following had been demonstrated:

- Conducted investigations to first understand and then resolve issues with platelets.
- Amorphous nature of alumina creates issues with fracturing film into individual platelets and dispersing resulting platelets.
- Magnesium Fluoride can be used as an intermediate layer in this study to facilitate fracture of individual platelets.
- Dispersing agents and probe-tip sonication can facilitate better dispersions.
- Demonstrated ability to manufacture hexagonal wavy platelets.
- Developed slip-casting die-pressing processing method to fabricate macroscale layered composite samples without need for heat (sintering).
- Successfully conducted HiPIPS investigations using HMDSO and VPADME.
- Characterized HiPIPS HMDSO and VPA plasmas using SIMS, OES, and electrical probes.
- Demonstrated capability to tailor plasma chemistry through control of HiPIPS processing parameters.
- FTIR, SEM, Auger, and XPS analysis of treated substrates and platelets confirm successful surface functionalization using HiPIPS HMDSO and VPA plasmas.
- Moreover, results indicate that vinyl and phosphonate groups survive HiPIPS VPA induced fragmentation.
- Demonstrated versatility of HiPIPS to provide a variety of precursor chemistries.
- Designed and fabricated 1 foot wide linear source.
- Verified operation of 1 ft linear HiPIPS using Ar. Compared linear HiPIPS Ar plasma with DC operation.
- Demonstrated operation of 1 ft linear HiPIPS with HMDSO and VPA precursors.
- Demonstrated scalabiity of HiPIPS through application of HMDSO and VPADME plasmas to ~1,500 ft of roll-to-roll process manufacturing ~150g of functionalized platelets.
- FTIR confirmed surface functionalization and reliability in roll-to-roll process.
- Demonstrated scalability of HiPIPS with source designs that range from 1 mm (for integration with laser based technologies) up to 1 foot wide (for application to roll-to-roll deposition process).
- Executed a subset DOE to evaluate effect of HiPIPS surface treatment on platelet interfaces on resulting macroscale mechanical properties.
- Fabricated samples and conducted 3-point bend testing.
- 3-point bend test suggest HiPIPS HMDSO and VPADME surface treatment of platelet to tailor interfacial properties improved mechanical properties.
- HiPIPS VPADME treated samples exhibit 100% increase in strength and toughness as compared to untreated samples.

5 CONCLUSIONS

A large scale, thin film and surface treatment process using a novel High Power Impulse Plasma Source (HiPIPS) was developed that promoted interfacial adhesion and thus improved mechanical properties of layered composite materials. The team 1) demonstrated the function of HiPIPS to dissociate molecular gas precursors for thin film deposition and surface modification processes; 2) demonstrated of scalability of HiPIPS through application to a 1 foot wide roll-to-roll process; 3) developed and executed of an experimental design for a multi-dimensional layered composite materials test bed that examined molecular through macro-scale mechanisms on resulting structure-property; and 4) demonstrated of HiPIPS ability to tailor surface interfacial chemistry for improved properties through investigation in a multi-dimensional test bed for manufacture of layered composite materials.

REFERENCES

[1] (a) E. Munch, et al, "*Tough Bio-Inspired Hybrid Materials*," Science, **322**, 1516, (2008).(b) Katti, D. R., S. M. Pradhan & K. S. Katti (2004) *Reviews on Advanced Materials Science,* 6**,** 162-168.(c) Tang, Z. Y., N. A. Kotov, S. Magonov & B. Ozturk (2003) *Nature Materials,* 2**,** 413-U8.

[2] (a) Phillips, R. W.; Mayer, T.; Ash, S. US Patent 5135812, March 27, 1991. (b) Rauchmann H. W. US Patent 6317947, November 9, 1988. (c) Wavefront Technologies, Inc. Website. http://www.wft.bz/ Accessed 18 April 2014.