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USING ADDITIVE PROCESSING TO HARNESS AND IMPLEMENT GRAPHENE TECHNOLOGY FOR WEAR AND CORROSION PROTECTION

EXECUTIVE SUMMARY

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Project Summary

Graphene is an amazing two-dimensional material that has garnered much attention since it was first fabricated nearly 20 years ago. Since its discovery in 2006, scientists and engineers have attempted to find applications of graphene, both standalone and as part of a composite material, to bring the nanomaterial to market. As of 2022, nearly 20 different products have come to market taking advantage of one or more of graphene's amazing properties, e.g., use as a flexible touch screen for smartphones due to its high electrical conductivity, stiffness, and optimal optical properties. This study focused on using graphene in both a polymer matrix composite and in an aluminum cold-sprayed coating. Graphene was added to a common polymer, polyethylene terephthalate glycol (PETG), to improve its hardness, wear resistance, and ultraviolet (UV) resistance. The nanomaterial improved the hardness and wear resistance but experienced greater degradation when exposed to UV-B radiation at high temperature and humidity. Graphene was also added to aluminum (Al) powders, which were then cold sprayed onto an aluminum substrate. The graphene improved the hardness and adhesion strength of the coating but saw reduced wear resistance. Both effects were attributed to the interaction of the graphene with the Al "splats" in the coating. Improvements to wear resistance was observed in PETG but not in the Al composite coating. The Al composite coating exhibited small improvement in adhesion strength and hardness. Increasing the amount of graphene in these composites may further improve the mechanical properties of the composite materials.

Keywords: *graphene*, *additive manufacturing*

Background

The overall objective of this study was to analyze the potential of graphene-based materials, like graphene nanoplatelets (GNP), for use in naval applications. Of specific interest was the use of GNP in protective coatings for ship hulls, fuel tanks, or other parts that are exposed to severe wear and corrosion damage. If graphene can enhance resistance to wear and corrosion, while minimally or even positively impacting cost, then the technology could be ripe for transition to the fleet. Of the several specific research objectives, the first was to investigate any environmental concerns to marine life or health implications of using graphene-infused material. The second objective was to study the cost-benefit of adding graphene to materials and the marketability of these composites. The third objective was to validate the incorporation of GNP to additive manufacturing processes like fused deposition modeling or cold spraying. A fourth objective was to analyze any changes to the microstructure and mechanical properties of graphene-infused coatings or 3D-printed polymer parts and whether the GNP enhance resistance to wear and/or corrosion.

A literature review was conducted to investigate possible toxicity and cytotoxicity of graphene-based materials like GNP. The scope of this review included graphene released to waterways and the soil and any possible effects. Another review of case studies of the cost-benefit of adding graphene to products brought to market was conducted. For objectives three and four, a polymer, PETG, and a metal coating, Al, were chosen. PETG pellets were mixed with GNP (no more than 1 vol%) in a Felfil filament extruder. Composite filament was then used to print 5 cm x 5 cm x 3 mm samples. For Al, GNP (this time 2 vol%) were mixed with Al powder using a high energy ball miller. The composite powders were then cold sprayed onto an Al-6061 substrate. After the substrates were sprayed, they were heat-treated at 400 °C for 20 minutes in an inert argon atmosphere.

Once printed, polymer samples were wear tested in a Nanovea T50 tribometer using 3 mm stainless steel balls to wear down the surface. Three one-hour wear tests were performed on each sample. Once complete, the PETG and PETG-GNP samples were examined in a scanning electron microscope (SEM). Cold-sprayed Al and Al-GNP samples were also wear tested with similar parameters to the polymer samples. The metal samples also underwent micro- and nano-indentation testing and adhesion strength testing. Adhesion testing left a fracture surface in each sample. The fracture surface and a cross-section of the fracture surface from each sample was investigated with both an optical microscope and a SEM.

Findings and Conclusions

There are several ways for graphene to enter the environment. The most likely avenues are application of graphene as an absorbent for cleaning fluids of metals and molecules. The graphene would be released and contribute to cleaning a waterway, for example. Removal of the graphene, however, would be difficult. Graphene could also enter soils and, subsequently, waterways. When in the soil, the graphene may interact with the nutrients and chemicals, changing the pH and affecting the soil ecology. Research in this topic is still nascent, and the extent of the effects of graphene and its derivatives in the environment is yet undetermined.

The small addition of GNP to PETG greatly reduced the transparency of the polymer, which was received as clear filament from the manufacturer. Some of the samples were then exposed to UV-B radiation at higher temperatures and humidity to accelerate the polymer's aging. The polymer microstructure was examined, and samples were wear-tested. The composite polymers exhibited higher wear resistance before accelerated ageing. Wear width was smaller and wear depth shallower in the PETG-GNP sample compared to the PETG sample. This was reversed with the samples exposed to UV/heat/humidity. The composite had a wear track 35% wider and 25% deeper than the exposed PETG sample.

For the Al-GNP system, the composite coating showed lower porosity; however, the coating was thinner compared to the control Al coating. The cause was likely due to clogging of the cold spray nozzle. When spraying with the composite powders, the nozzle would clog due to GNP depositing on the interior surface of the nozzle. The micro-indentation hardness of the Al-GNP was 75% higher than the pure Al coating, while the difference in nano-hardness and elastic modulus were negligible. The Al-GNP also had smaller variance in nanoindentation tests. Plasticity was indistinguishable for the two coatings. The micro-indenter creates a larger indent with a larger load of the surface, increasing the chances of indenting splats with attached GNP. The chances of this happening with the nano-indenter were low in comparison. The nano-indenter hit a larger proportion of bare matrix material, measuring values closer to that of the Al. The wear loss in the GNP sample was 300% higher than the loss found in the Al coating. Further, the wear depth was 50% deeper. Despite the improvements in the hardness, the decrease in wear resistance of the composite coating is also due to the GNP's presence. Because of the bridging of splats by the GNP, when a splat comes loose from the bulk, it brings along a single graphene platelet. So, instead of lubricating the surface as graphene normally does in cases of frictional relief, the splat/GNP combination contributes to wear of the surface.

Recommendations for Further Research

Despite these mixed results, the amount of graphene nanoplatelets (GNP) in both composites were low and, unlike carbon nanotubes, GNP are easier to disperse during mixing. So, a higher concentration of GNP should be possible and may lead to greater improvements in mechanical properties. Further research should focus on increasing the amount of GNP introduced into the composite while also ensuring good dispersion of the nanoparticles. Although aluminum was considered as the metallic matrix composite coating in this study, other sprayed metals like copper or its alloys may benefit from the addition of GNP in terms of wear and corrosion resistance.

Acronyms

Al	aluminum
GNP	graphene nanoplatelets
PETG	polyethylene terephthalate glycol
SEM	scanning electron microscope
UV	ultraviolet