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GRAPHENE-PEEK COMPOSITES AS MICROWAVE-ACTIVATED HIGH-TEMPERATURE ADHESIVES

Proceedings of SAMPE's 2018 Spring Technical Conference and Exhibition
May 21-24, 2018
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14. ABSTRACT

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ABSTRACT

Polyetheretherketone (PEEK) is a widely used engineering polymer that is especially suitable for high-temperature applications. Graphene is a two-dimensional form of carbon nanomaterial that has been studied extensively for its mechanical, electrical and thermal properties and its use as a filler in polymer matrices. Compounding graphene into polymers has the potential to improve various properties, even at very low concentrations. In this work, we have examined the incorporation of graphene nanoplatelets (GNP) into PEEK by fabricating composites using melt-mixing techniques, as well as by graphene functionalization and in-situ polymerization of the PEEK. In this way, we can compare the performance of the composites by two different processing methods. To examine mechanical properties and the viability of the composite as an adhesive, lap-shear joints using the GNP-PEEK as the adhesive were fabricated and mechanically tested. Results show that the weight fraction of GNP has a major effect on the strength of the joint. A 70% increase in lap-shear strength is demonstrated for the 2 wt% GNP composite, as compared to the pure PEEK joints. In addition to the PEEK-GNP composites, lap shear samples were fabricated via 3D printing, with a layer of carbon nanofiber (CNF)-PLA printed as the adhesive. In this work, we aim to produce a material that functions as a reusable high-temperature, thermoplastic adhesive, which can be activated by conventional heating methods, or by microwave heating. Microwave heating allows only localized melting of the adhesive joint where the microwave absorbers are present (GNPs or CNFs). The GNPs and CNFs absorb microwaves and heat the surrounding polymer matrix to the point of melting, in contrast to the neat polymer, which does not melt upon exposure to the microwaves under the same parameters. The dielectric and microwave absorption properties, as well as the adhesive properties of these advanced materials will be presented.

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1. INTRODUCTION

Joining of composites can be a challenging issue. If adhesives are used, the joints are permanent and cannot be undone. If they need to be undone, inserts are often used and these inserts increase cost and weight. Additionally, fibers can be cut in the process leading to a part with weakened mechanical properties. Even with these drawbacks, most components that need to be joined are threaded together, allowing for removal of the parts at a later time. However, threaded connections are costly to design and manufacture, and are often the location of fatigue failures due to their inherent stress concentrations. From an environmental and cost standpoint, there is a large waste associated with the removal of material to form the threads, even more so in sectored threads, where up to half of the machined thread is then cut away. Additionally, threaded joints often require grease to seal out environmental contamination and ensure that they can later be disassembled. This effort is aimed at replacing seldom-used threaded connections with a reusable thermoplastic adhesive.

The use of a thermoplastic makes the joining reversible, allowing any connection to be treated almost like a threaded joint, only one that uses heat instead of torque for activation. Recently, using thermoplastics as reusable adhesives has been researched by DoE for application in automobiles [1]. However, that work is focused on thermoplastics for room temperature applications, with no work being conducted on high temperature thermoplastics such as PEEK and Polyimide. The use of localized microwave radiation to heat the thermoplastic will eliminate the need for large furnaces which consume large amounts of time and energy, and ultimately heat other parts of the system that do not need to be heated. Our laboratory has begun investigating activation of high temperature thermoplastics using microwave radiation.

Figure 1 shows the basic concept. Two adherends are brought together with a graphene-doped thermoplastic between them. The assembly is then subjected to microwaves which excite the graphene nanoplatelets in the adhesive generating heat and causing the adhesive to melt. When the microwave source is removed, the adhesive solidifies joining the two materials. Since the adhesive is a thermoplastic, subsequent applications of microwaves can be used to re-melt the adhesive and disassemble the assembly. For adherends that block microwaves, a wave guide would be needed to direct them to the bondline.

While various carbon species can absorb microwaves [2], nanospecies such as carbon nanotubes and graphene have been investigated most recently [3-5] because of their highly effective absorption at low weight loadings and ability to improve mechanical properties as well. Microwaves, when incident on an absorptive material, create heating by the interaction of the electromagnetic fields with the molecular and electronic structures of the molecules in the material exposed to the microwaves. The amount, and rate, of heating can be a function of microwave power, frequency, absorption, etc. We aim to study all these factors as we investigate microwaves as a heating source for high-temperature, reusable thermoplastic adhesives.

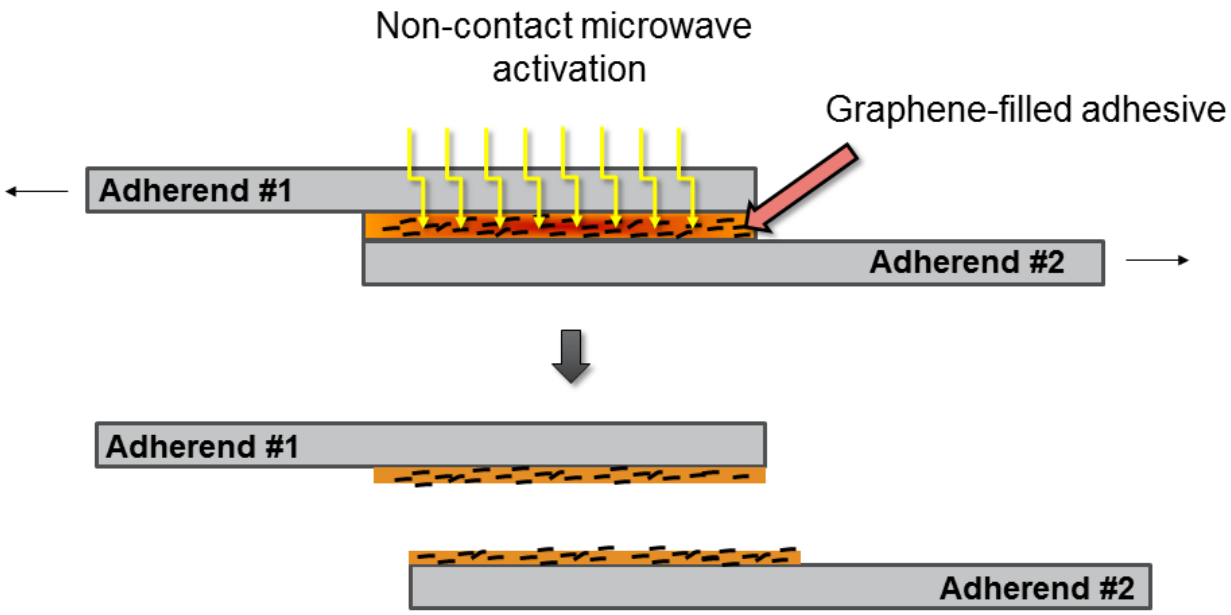

Figure 1: Schematic representation of the concept.

2. COMPOSITE PREPARATION

Melt-mixed GNP-PEEK composites, in-situ polymerized GNP-PEEK and graphene-PEEK composites have all been made. Dry powders of PEEK (Solvay Ketaspire KT-820FP, Tm = 343 °C, Tg = 143 °C) and 1 wt% graphene nanoplatelets (XG Sciences, Grade M) were mixed using a high speed mixer (Flacktek). GNPs are thicker (6-8 nm) than single or few-layer graphene (less than 1 nm). This uniformly mixed material was then melt compounded using a Haake torque rheometer. This is an intensive mixer with two counter rotating rotors and a temperature controlled barrel [6]. In addition to melt-mixing method, we have prepared composites using in-situ polymerization of the PEEK in the presence of GNP and few-layer graphene (functionalized and non-functionalized), which is described in more detail below. By studying various graphene species and fabrication methods, we will be able to select which method shows the best performance.

3D printed composites of polylactic acid (PLA) and PLA/carbon nanofiber (CNF) were fabricated. A commercially available material was used but the vendor would not disclose the weight percentage. Based on SEM images it appears to be above 10 wt%. An Ultimaker 3 dual extrusion 3D printer was used. Several types of samples were printed. Full assemblies of adherend and adhesive were printed as well as individual pieces. Additionally solid PLA examples of the lap shear samples were printed. In all cases the dimensions were identical and parts were printed in a horizontal orientation. For the separately printed pieces, the three pieces were taped together and placed in a microwave for bonding. The bonding process took 3 – 5 seconds in a commercial (780W, 2.45 GHz) microwave. Arcing, sparking and occasional flame was noticed during the bonding. The appearance of large sparks / flames is when the process was stopped. Additionally two samples with a printed PLA/CNF joint was microwaved for 5

seconds and the joint was opened. After cooling the joint was repositioned, taped closed and microwaved to re-bond the joint. This can be seen in Figure 2.

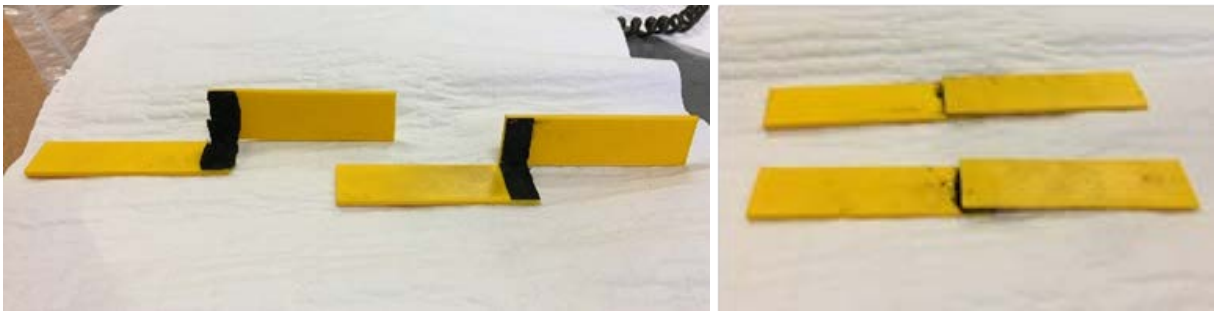

Figure 2: Rebonded PLA/CNF Joint.

3. IN-SITU POLYMERIZATION OF PEEK

3.1 Functionalization of Graphene

Safety warning: The functionalization reaction makes use of an in situ diazonium salt. Diazonium salts are explosive and appropriate safety measure must be used for this reaction.

N002-PDR graphene (Angstron Materials) with specific surface area of 600 m^2/g and, thus, approximately 46% surface exposed carbons atoms was used for functionalization. A round bottom flask was loaded with N002-PDR graphene (150 mg, 1eq surface) and 4-aminophenonl (2.51g, 2 eq). The flask was purged with argon and anhydrous tetrahydrofuran (50 mL) was added to the flask followed by iso-phenylnitrile (3.1 mL, 2eq). The reaction was allowed to proceed at 50°C for 22 h. The functionalized graphene was collected by centrifugation and washed with hexanes and ethyl acetate.

3.2 PEEK Polymerization with Functionalized and Non-Functionalized Graphene

A microwave synthesis vial (30mL) was loaded with hydroquinone (1.10g, 1eq), 4,4'-diflourobenzophenone (2.18g, 1eq), sodium carbonate (1.17g, 1.1eq), and functionalized graphene or graphene nanoplatelets (30mg, 1% wt product). 1-butyl-3-methylimidazolium bis[(triflouromethyl)sufonyl]amide (5 mL) was added to the vial. The vial was sealed and the reaction was carried out using a Monowave 400 microwave synthesizer (Anton Paar) at 300°C for 30 minutes using a ruby thermometer for temperature control. The resulting product was collected by centrifugation and washed by resuspension and centrifugation ten times alternating between water and acetone.

4. EXPERIMENTAL METHODS

4.1 Material Characterization

The composite materials were characterized using various methods. Electron microscopy (FEI Nanolab 600i) was performed on the samples in order to characterize the dispersion quality of the GNP and few-layer graphene in the composites. Thermogravimetric analysis (TGA, TA Instruments TGAQ50) and Differential Scanning Calorimetry (DSC, TA Instruments DSC Q100) of the in-situ polymerized PEEK with 1 wt% functionalized graphene was performed in order to study the degree of PEEK formation and interaction with graphene. We then perform a series of microwave absorption tests on the polymer and composite materials. In the first tests, we present qualitative results demonstrating how the graphene absorbs microwaves and melts the PEEK. These tests are performed in a commercially available microwave appliance (780W, 2.45 GHz). Additional relative permittivity and insertion loss measurements were performed from 2 to 4 GHz with a Model M07T 7mm coaxial fixture using an Anritsu 4647B vector network analyzer under control of MU-EPSLN™ for Mac OS X. These tests give a quantitative description of microwave absorption to supplement the qualitative results.

5. COMPOSITE CHARACTERIZATION

5.1 Microstructure Analysis

Figure 3 shows the 1 wt% GNP melt-mixed in the PEEK. Nanoplatelets are clearly seen in the fracture surface. Figure 4 shows the microstructure of PEEK-GNP (Figure 4a) and PEEK-functionalized graphene (Figure 4b), where the PEEK has been formed by in-situ polymerization. The PEEK is polymerized around the GNP, and it is believed to polymerize off of the functional groups in the case of the functionalized graphene. PEEK that is attached to the graphene through a functional group is expected to show improved thermal and mechanical properties, and perhaps, increased microwave absorption and heat transfer to the polymer. Microstructures of the PLA/CNF printing filament are show in Figure 5. The filament was fractured and CNFs that are approximately 200 nm in diameter are shown protruding from the fracture surface.

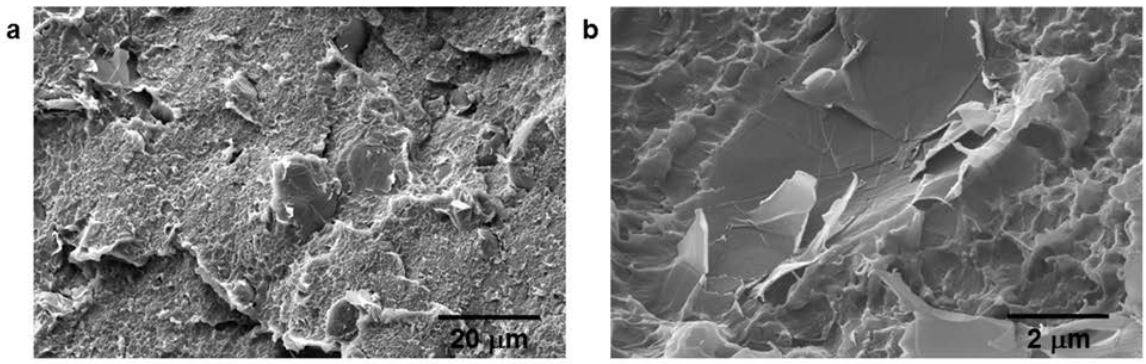

Figure 3: a) Electron microscopy image of 1 wt% GNP dispersed in PEEK. b) Higher magnification of GNP on the surface, where the layered structure of the carbon sheets is clearly seen.

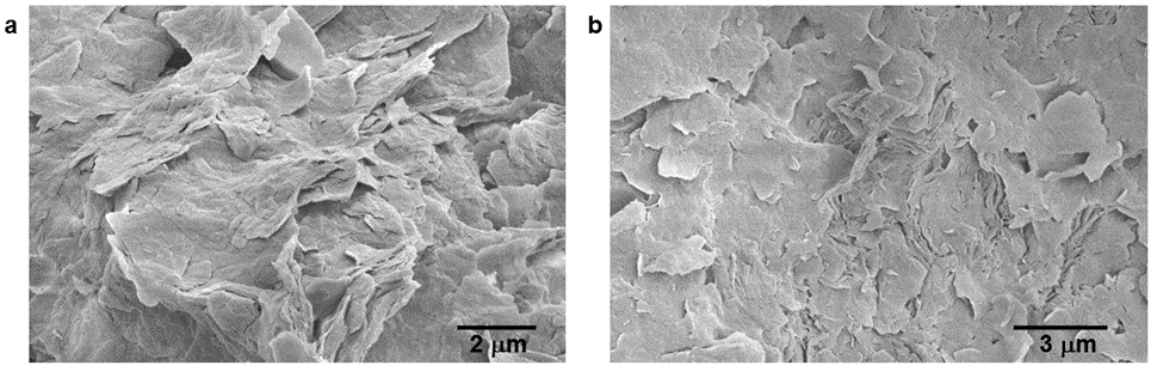

Figure 4: a) Electron microscopy image of 1 wt% GNP in PEEK, where the PEEK was formed by in-situ polymerization and b) 1 wt% of functionalized few-layer graphene in PEEK, where the PEEK was formed by in-situ polymerization.

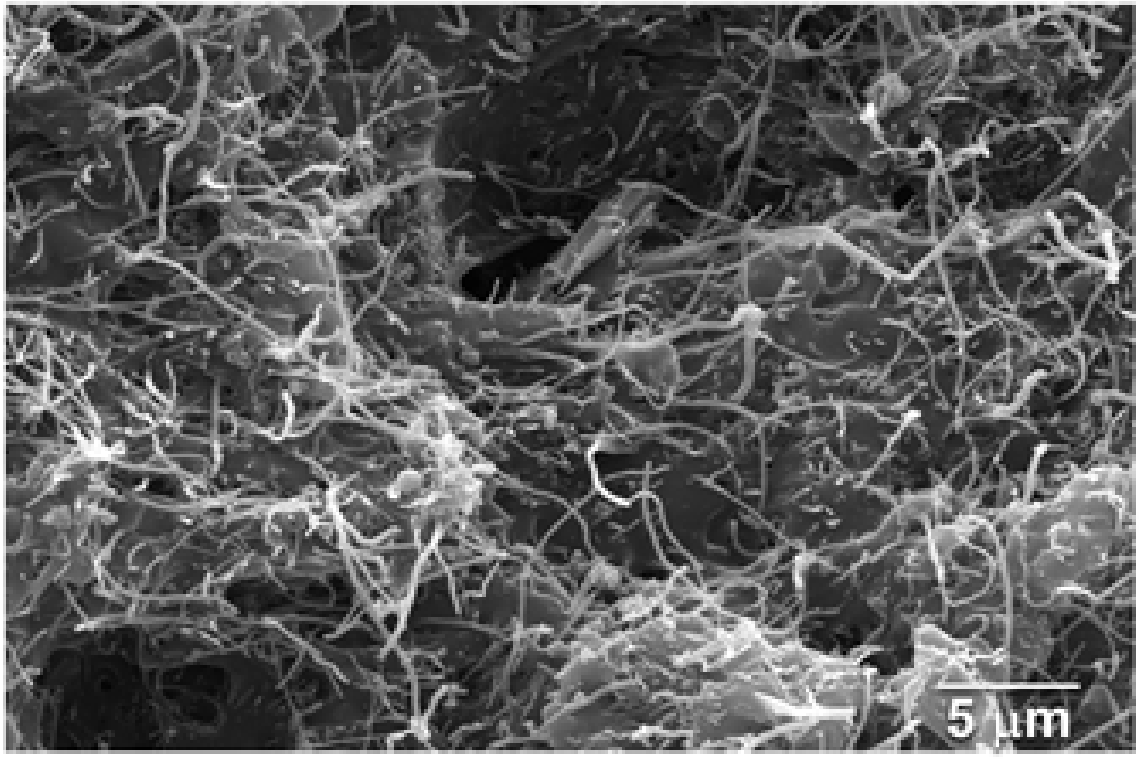

Figure 5: Carbon nanofibers protruding from the PLA filament.

5.2 TGA/DSC

Thermogravimetric analysis and Differential Scanning Calorimetry of the in-situ polymerized PEEK with 1 wt% functionalized graphene and 1 wt% GNP is shown in Figure 6. Both tests were conducted in a nitrogen atmosphere and heated at 5 °C/min and cooled at 20 °C/min. The high char content (residual weight % at 1000 C) shows that the polymerization was successful in creating high molecular weight polymer chains [7]. The results also show that the functionalized graphene adds thermal stability (TGA curve shifted to the right) to the polymer. These preliminary tests indicate that the functionalized graphene could provide improved properties to the polymer compared to the larger GNP. The cooling curves for DSC are shown in Fig. 6b. The functionalized graphene material shows a solidification exotherm at 245 °C and the GNP composite shows one at 232 °C. The GNP shows a larger crystallization exotherm at 163 °C, and the graphene composite shows little-to-no exotherm at this temperature. This could be a result of the well-dispersed, high surface area graphene interacting with the polymer chains and creating a steric hindrance effect, where the PEEK chains do not have the mobility to move and form crystallites. This could result in competing effects during microwave exposure, where high absorptivity and heat transfer may lead to faster localized melting, but lower chain mobility delays bulk melting. These factors will be studied in more depth during future work.

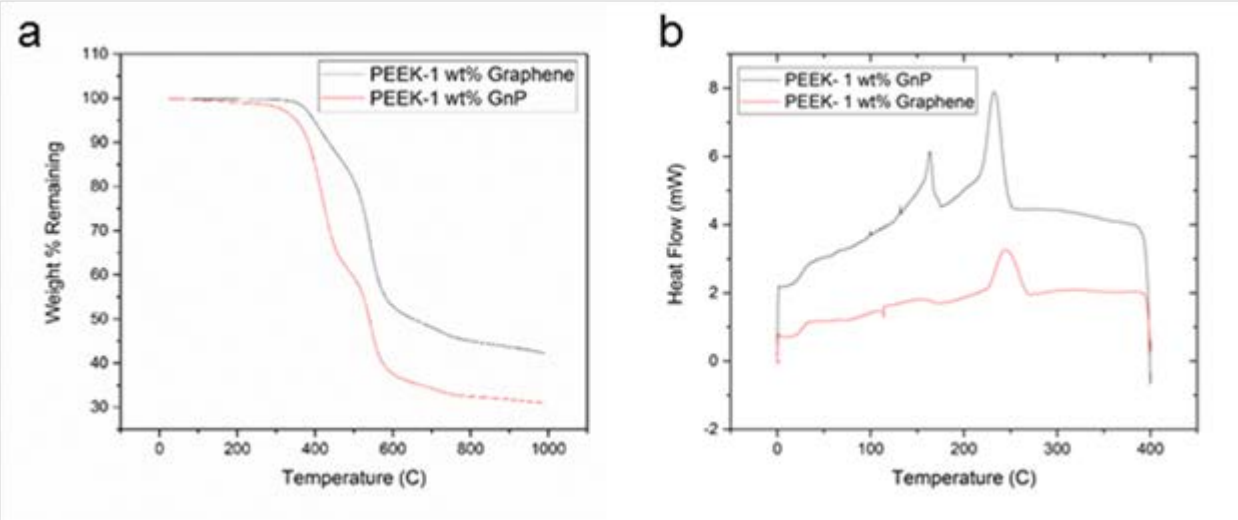

Figure 6: a) TGA of polymerized PEEK with 1 wt% functionalized graphene and PEEK with 1 wt% GNP. b) DSC of polymerized PEEK with 1 wt% functionalized graphene and PEEK with 1 wt% GNP.

5.3 Microwave Response Characterization

Proof-of-principle melting tests were conducted to observe the response of PEEK-GNP and PLA/CNF composites when exposed to microwaves.

Pure PEEK and 1 wt% GNP-PEEK was placed in a commercial microwave (1250W, 2.45 GHz) oven to see which would melt first. The 1 wt% GNP-PEEK melted after tens of minutes. The pure PEEK did not melt before the test was stopped due to the turntable rotor melting (a low temperature plastic). Figure 7 shows 1 wt% GNP-PEEK (black, melted) and pure PEEK (white powder, no melting).

In another test, we studied the microwave exposure of higher GNP content PEEK composites in a commercial microwave oven (780W, 2.45 GHz). Here, we see the 35 wt% sample begin to melt and ignite into flames within just a few seconds exposure. The 10, 5 and 2 wt% samples began to show bulk melting and bubbling by 2:56, 3:30 and 4:15 minutes, respectively. All samples (except the 35 wt%) had similar volumes. The samples, after melting, are shown in Figure 8. The time to bulk melting decreases linearly with the amount of GNP in the composite.

It is clear that the amount of GNP in the composite has an effect on the microwave absorption behavior. Other factors that can play a role in absorption behavior are graphene type (platelet versus mono- or few-layer), degree of dispersion, functionalization, etc. Studying these factors in PEEK nanocomposites is a current topic of research in our laboratory.

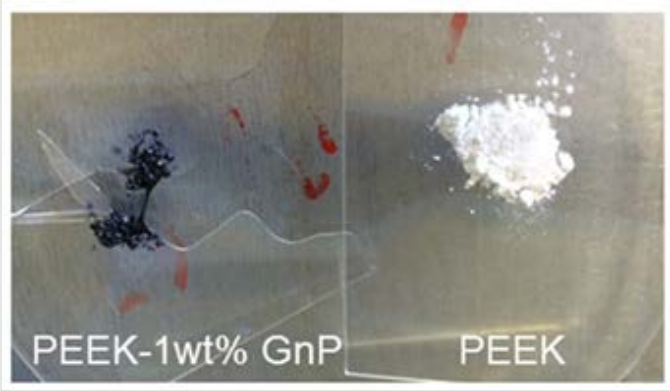

Figure 7: 1wt% GNP-PEEK (melted black material) and Pure PEEK powder (white) exposed to microwaves.

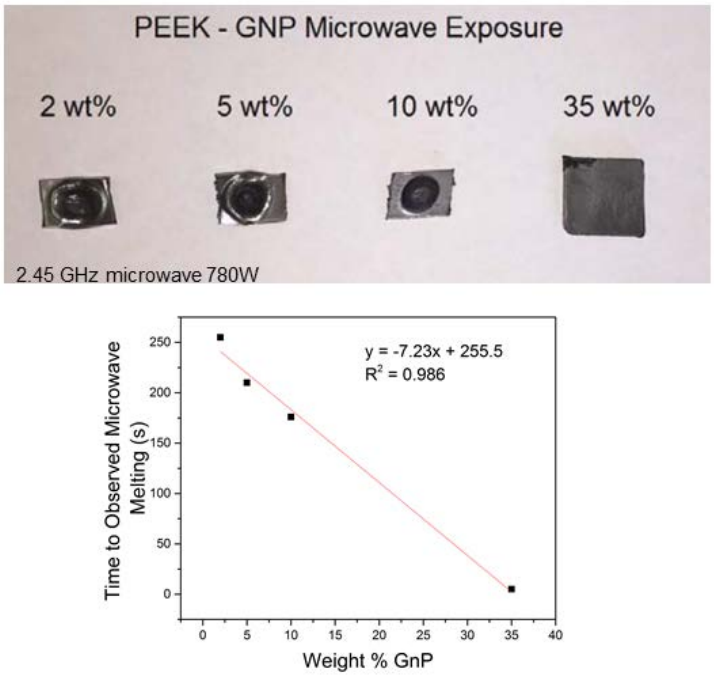

Figure 8: High-weight fraction PEEK/GNP composites after exposure to microwaves. The 2, 5 and 10 wt% samples show bulk melting (center of specimens), while the 35 wt% shows melting/charring in the top left-hand corner. A graph of the time to observed melting for each sample.

The microwave response characteristics give a quantitative description of microwave absorption of the graphene composites, dielectric properties testing of the samples was conducted. Permittivity (real part - ε'), Permittivity (imaginary part - ε"), insertion loss, and tan $\delta = \varepsilon''/\varepsilon'$ data is shown in Figure 9. As the amount of GNP increases, the imaginary part of the complex relative permittivity increases, which is a measure of the energy loss in the material when subjected to microwave energy. The loss tangent tan δ, which is a ratio of the imaginary and real parts, is a measure of energy loss in the material and it also increases with increased GNP

content. The 35% GNP material shows high loss and also begins to act metallic. Conductivity tests showed that the 35% GNP had high electrical conductivity.

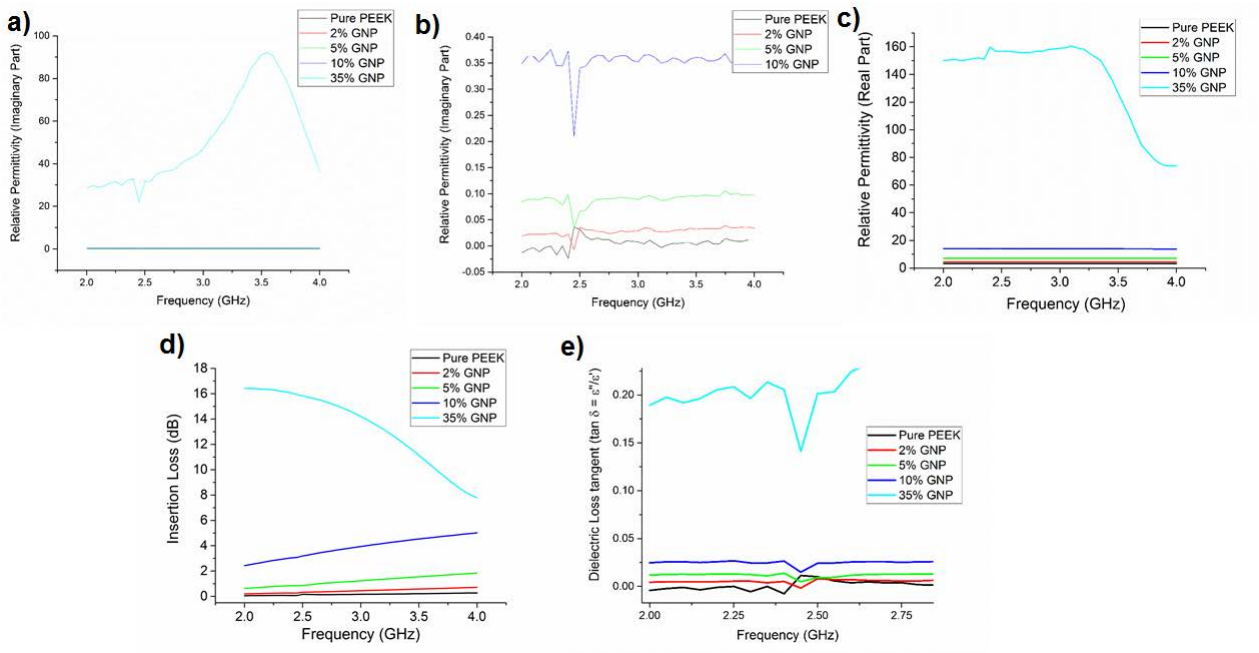

Figure 9: Dielectric testing results for Pure PEEK and GNP composites a) Relative permittivity (imaginary part), b) Relative permittivity (imaginary part) zoomed in, c) Relative permittivity (real part), d) insertion loss, e) dielectric loss tangent.

6. LAP SHEAR TESTING

6.1 Aluminum Samples

A standard test for assessing the performance of an adhesive is a lap shear test. In this test, two adherends are bonded together with a known overlap area and then pulled apart. We followed ASTM D1002 [8] for the testing and utilized aluminum adherends. The samples were made by taking two 203.2 mm (8 in) wide by 101.6 mm (4 in) long sheets of 2024 aluminum and overlapping them by 12.7 mm (0.5 in) in the 101.6 mm direction. In this overlap area a film of the adhesive was placed between the sheets. The assembly was then placed in platen press and heated to 357 °C (675 °F) at which time the pressure was increased to 2 MPa (290 psi) and then allowed to cool to room temperature. The plate was then sliced into a series of 25.4 mm (1 in) wide specimens.

A total of seven specimens using pure PEEK, 1, 2, 5, 10 and 35 wt% GNP PEEK composites were fabricated in this way. Measurements of the individual specimen's dimensions and overlap area and thickness were taken. The specimens were then tested to failure using an Instron tensile test machine (Figure 10). Calculations were done according to ASTM D1002 to calculate failure strength. The results are given below in

Table **1** and plotted in Figure 11.

Figure 10: Lap shear specimen in the Instron.

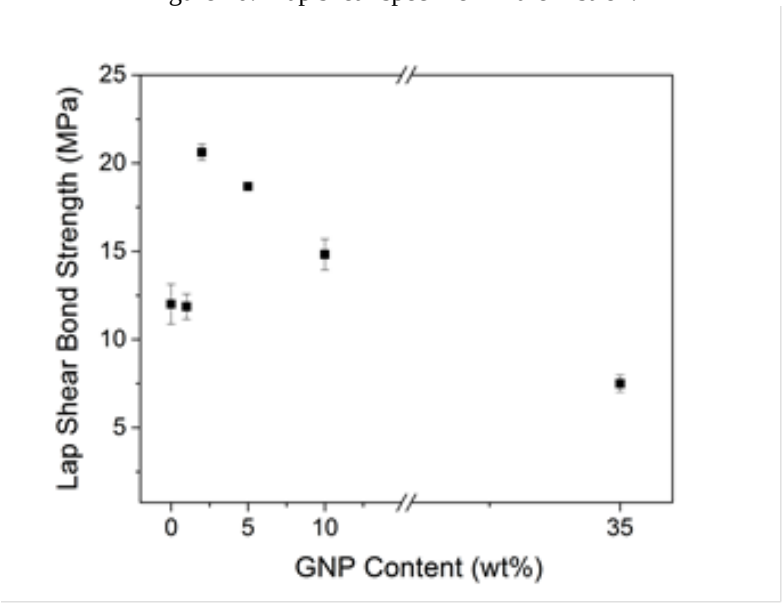

Figure 11: Plot of the lap shear strength of the PEEK-GNP adhesive lap shear joints. The 2.0 wt% GNP adhesive showed the highest strength.

Table 1: Results of Lap Shear Testing

Material	Failure Strength	Standard Deviation
PEEK	12.00 MPa (1.74 ksi)	1.10 MPa (0.16 ksi)
PEEK- 1 wt% GNP	11.86 MPa (1.72 ksi)	0.48 MPa (0.07 ksi)
PEEK- 2 wt% GNP	20.68 MPa (3.00 ksi)	0.46 MPa (0.067 ksi)
PEEK- 5 wt% GNP	18.68 MPa (2.71 ksi)	0.21 MPa (0.031 ksi)
PEEK- 10 wt% GNP	14.82 MPa (2.15 ksi)	0.88 MPa (0.127 ksi)
PEEK- 35 wt% GNP	7.51 MPa (1.09 ksi)	0.47 MPa (0.068 ksi)

Statistically, we see no difference between the 1 wt% GNP and pure PEEK. One possible reason for this is that the pure PEEK was purchased as a film whereas the 1 wt% was converted from extruded pieces to a film by repeatedly melting and compressing it on a heated platen press. This may have caused irregular dispersion of the graphene, porosity or uneven film thickness. The 2 wt% GNP composite shows the highest lap shear strength of all the samples (3.0 ksi), with a 72% improvement in strength over the pure PEEK joint. The 5 and 10 wt% GNP composites display a lower strength than the 2 wt% GNP, but are still higher than the pure PEEK. The highest weight fraction, 35 wt% GNP, shows a lap shear strength 38% lower than the pure PEEK.

After the test, the failure mechanisms of the samples were investigated. In all cases, the failure was cohesive with failed adhesive being evenly split between the two adherends, Figure 12 shows a PEEK (left) and 1 wt% GNP-PEEK (right) sample after failure. Figure 13 shows SEM images of the cohesive failure region with clearly visible graphene nanoplatelets. In Figure 13, SEM of the fracture surfaces for the 1 and 35 wt% samples are shown. While GNPs can be seen on both surfaces, the 35 wt% had large GNPs (hundreds of microns in size) on the surface. The platelets that are parallel to the lap shear direction contribute very little to the strength of the joint. Since weak van der Waal forces bond the graphene sheets together, large GNPs are easily sheared in the direction of the lap shear, which is evident in fracture surface images of Figure 13c and Figure 13d.

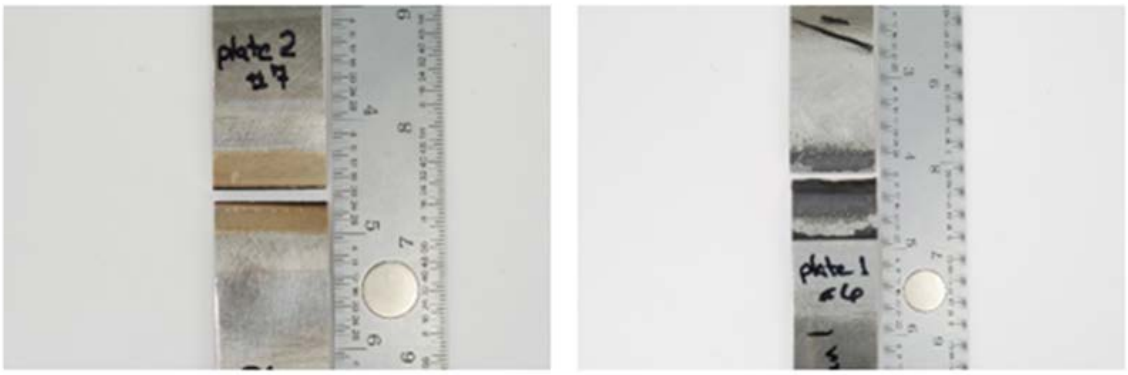

Figure 12: Lap shear specimens of pure PEEK (left) and PEEK-1wt% GNP (right) after failure.

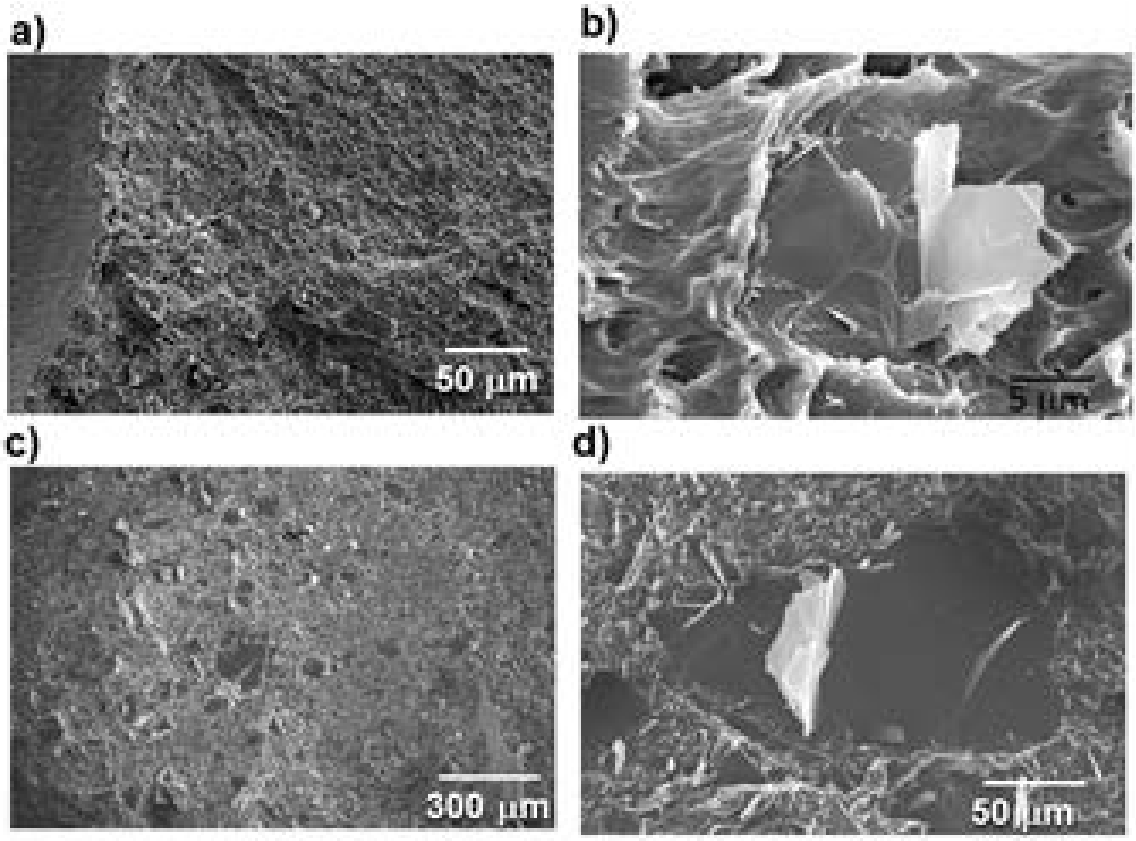

Figure 13: SEM images of the cohesive failure region with clearly visible graphene nanoplatelets. a) 1 wt% GNP sample b) a higher magnification of GNP in the 1 wt% sample c) low magnification SEM of 35 wt% GNP sample showing large areas of sheared GNPs d) Higher magnification of a GNP in the 35 wt% lap shear sample.

6.2 3D Printed Samples

Three primary types of 3D printed samples were tested: solid PLA, printed PLA/CNF joint, and microwave bonded PLA/CNF joint. Additionally, a sample that was de-bonded / re-bonded was also tested as a comparison. All samples were tested on the same Instron and under the testing profile as the aluminum/ PEEK-GNP samples. Figure 14 shows the samples and Figure 15 the average failure loads.

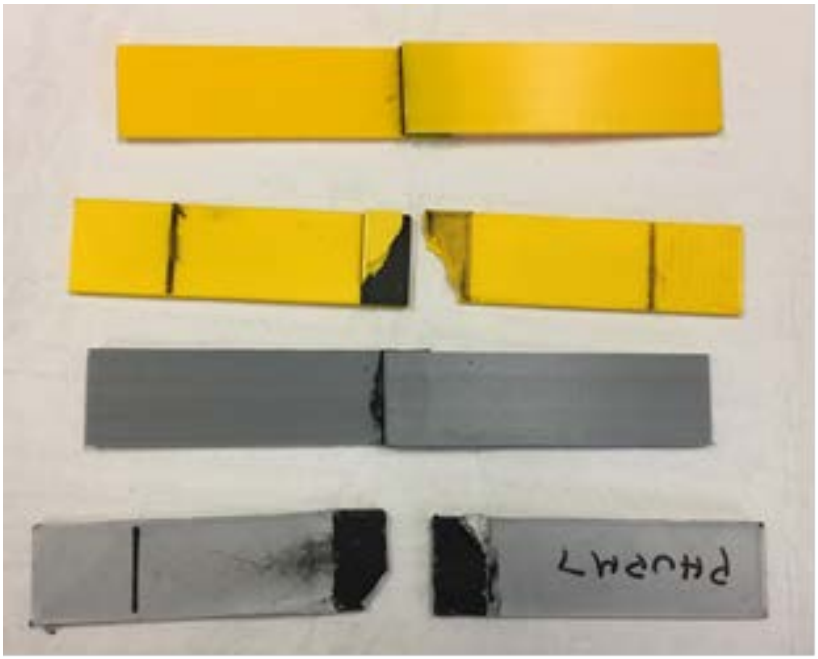

Figure 14: 3D Printed Lap Shear Samples – before and after testing. Top: Printed joint. Bottom: Microwave activated joint.

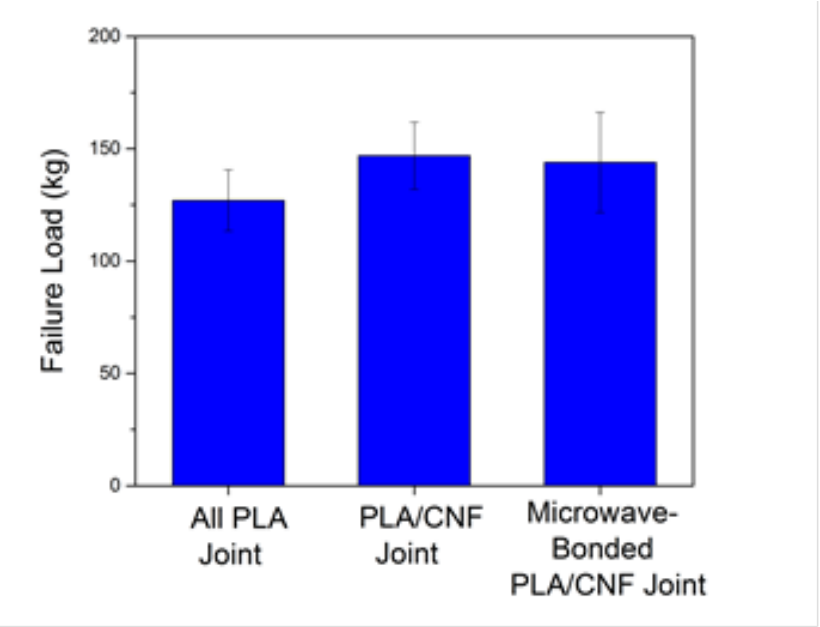

Figure 15: Failure loads of 3D Printed Samples for same bonded area.

The solid PLA samples all failed either just below or just above the joint and at an average load of 1.245 kN (279.941 lbf). The samples with a printed PLA/CNF joint failed at an average load of 1.442 kN (324.165 lbf). These failures were mostly adhesive (failure in the adhesive itself), with partial substrate failure. The one with the highest load though failed 90% in the substrate and only 10% adhesive. The average failure load for the ones with microwave bonded joints was 1.411 kN (317.316 lbf). There was no one dominant failure mechanism for these samples. Failure ranged from 100% substrate to 100% cohesive, with only one sample showing a small amount of adhesive failure.

Both sets using PLA/CNF joints being higher than the pure PLA samples is possibly due to internal structure of the 3D printed parts or possibly the CNF are allowing for more deformation prior to failure. Both sets of the CNF/PLA joint samples having close to the same failure load shows that we can achieve good bond strength by using the microwave for bonding. The fact that printed joints were mostly adhesive and the microwave joined ones were a mixture of cohesive and substrate shows that joints are behaving differently. If a more controllable microwave source was used perhaps a better result could be achieved from the microwave joint.

The de-bonded / re-bonded joint samples held load but failed at lower loads. One failed at 573 N (128.763 lbf) and the other at 1.099 kN (2463.961 lbf). The lower load one failed cohesively and looks like the PLA/CNF layer may have been overheated during re-bonding. For the higher load sample the substrate split thickness wise at the joint and then failed through the thickness just outside the joint. This may indicate that the substrate was overheated and weakened during the bonding process.

7. CONCLUSIONS

In this study, we have examined various graphene species in PEEK as potential materials for a high-temperature adhesive. Preliminary microwave testing has shown that the graphene or graphene nanoplatelet composites can absorb microwaves to a level that will melt the PEEK, a property that could be useful in using microwaves as a localized heating source in a reusable thermoplastic adhesive application. Lap shear testing showed that the 2 wt% GNP had the highest lap shear strength, with a 72% increase in strength over the pure PEEK. The PEEK 35 wt% GNP showed the lowest strength of all the materials. Analysis of the fracture surface of the 35 wt% GNP material showed large areas of sheared nanoplatelets, up to hundreds of microns in size. These acted as points of weakness in the lap shear samples, leading to low joint strength. In addition, we show that in-situ polymerization is a viable option for fabricating PEEK-graphene composites. Further testing of these materials is needed to demonstrate the potential as a high-temperature adhesive material. Further mechanical and microwave absorption performance of PLA/carbon nanofiber material was studied. 3D printed lap-shear joints of the PLA adherends and PLA/CNF printed adhesive showed that joints of similar strength to printed ones could be obtained from microwaving the parts. The ability to de-bond and re-bond via microwave activation was also demonstrated.

8. ACKNOWLEDMENTS

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