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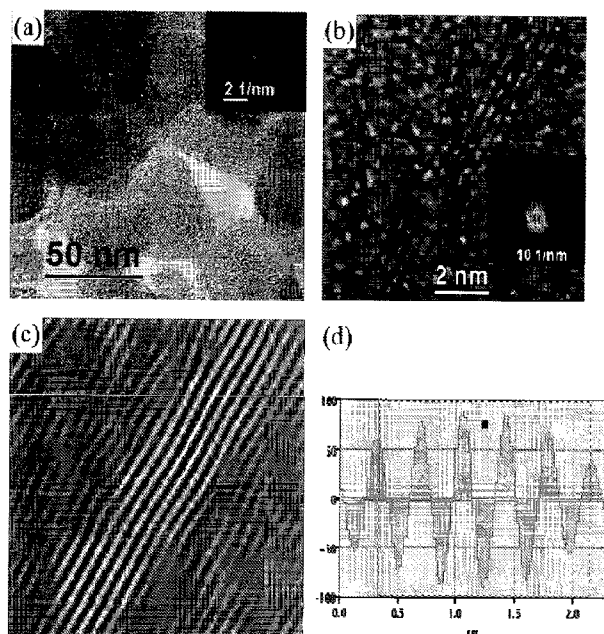


Fig. 2

(57) Abstract: A methodology is disclosed to produce nano-structured carbon particles that act as effective reinforcements. The process is conducted in the solid state at close to ambient conditions. The carbon nanostructures produced under this discovery are nanostructured and are synthesized by mechanical means at standard conditions. The benefit of this processing methodology is that those carbon nanostructures can be used as effective reinforcements for composites of various matrices. As example, are to demonstrate its effectiveness the following matrices were including in testing: ceramic, metallic, and polymeric (organic and inorganic), as well as bio-polymers. The reinforcements have been introduced in those matrices at room and elevated temperatures. The raw material is carbon soot that is a byproduct and hence abundant and cheaper than pristine carbon alternatives (e.g. nanotubes, graphene).



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SYNTHESIS OF CARBON NANOREINFORCEMENTS FOR STRUCTURAL APPLICATIONS

RELATED APPLICATIONS

[0001] This application claims priority to, and incorporates by reference, U.S. Provisional Application No. 61/970,026, filed March 25, 2014.

FIELD

[0002] The embodiments disclosed herein involve the development of novel carbon reinforcements. Those reinforcements are ideal for applications in composites. The reinforcement is effective for ceramics, polymers (organic inorganic, and bio-compatible), and metals. Therefore, this reinforcement can be used for any of the above mentioned matrices.

BACKGROUND

[0003] Carbon nanostructures as fullerene, nanotubes, and graphene have been widely used to reinforce different inorganic matrices (e.g. polymers (organic, inorganic and bio-), metals, concretes, ceramics, etc.) thus producing composites with improved mechanical or multifunctional properties. The most common polymer matrices include, epoxy, polyester, polyvinyl, pure carbon (graphene, amorphous, graphitic), polyethylene, etc. Carbon nanotubes have demonstrated mechanical improvements on polymers matrix composites such as strength, toughness, elongation, Young's modulus, wear. Further improvements are reported on conductivity, in both DC and AC modes. Proper functionalization of carbon nanostructures provides further enhancement of the mechanical properties of composites. In polymers, the interactions (i.e. chemical) among the reinforcement and matrix may result in further enhancement of the mechanical properties. Carbon particles (e.g. nanotubes or graphenes) can be the key to trigger polymeric matrices with multi-functional character for manufacturing of lightweight components for advanced applications (aerospace, electronics, automotive etc.). However, the literature highlights that a serious limitation in this type of composites is represented by the inefficient dispersion of the nanotubes in the host matrix.

[0004] Several efforts had been conducted to reinforce composites with carbon for decades. Carbon-carbon composites were first developed by introducing fibers in carbonaceous matrices known for their exceptional thermal shocks, wear, ablation, toughness, high temperature, and friction resistant properties. The fibers have strengths of up to 4 times that of advanced steels (up to 4 GPa). These composites are useful for aerospace, defense among other applications. Traditionally, the synthesis of carbon nanostructures (fullerene, nanotubes and graphene) is conducted by evaporation of carbon. Those carbon nanostructures are known for their outstanding mechanical electrical and thermal characteristics. The carbon nanotube opened new horizons for structural materials to reinforce textiles, polymers, metals and ceramics. On those early stages the hardness in metallic matrices had been improved in up to 800 %. More recent reports show toughness improvements in ceramic matrix composites between 300 % and 500% with electrical property improvements of more than 12 orders of magnitude.

[0005] The development of carbon nanostructures to reinforce composites is a strategy for producing a new generation of materials with superior mechanical properties. Carbon nanotubes are the most investigated particles with positive results. However, the improvements in mechanical properties are below theoretical expectations. Similar results are found with graphene. The scientific community has been using pristine quality carbon nanostructures to reinforce composites. Pristine quality carbon nanostructures possess outstanding properties; unfortunately, these properties are affected by the particle's integrity thereby limiting choice of manufacturing methods. Further, carbon nanotubes have discrete reinforcement effects. In order to achieve effective reinforcement it is necessary to develop an interconnected network of the reinforcement that guarantee intimate interaction with the matrix. The ideal carbon reinforcement should possess the following characteristics: 1) large surface area, 2) malleability, 3) resistance to thermo mechanical processing, 4) limited reactivity with the matrix, 4) easy to synthesize and manipulate, 5) in situ transformations into nanotubes, fibers, etc., and 6) potential for mass production and cost effective. From the above list the most important properties are mass production and the particle's ability to transform in situ in order to guarantee effective reinforcement.

SUMMARY

[0006] The embodiments of the invention disclosed herein relate to a method of synthesizing carbon nano-reinforcement material. In these embodiments, the method comprises the steps of obtaining fullerene soot with less than 10% by weight of fullerene and subjecting the soot to mechanical milling for between 0 and 50 hours to obtain a milled product.

[0007] Still further, in certain embodiments to synthesize a carbon nano-reinforcement material, the milled product is combined with at least one matrix powder.

[0008] In embodiments of the invention concerning the matrix powder, the matrix powder can be a metal, a ceramic, a glass, an inorganic polymer, an organic polymer, a bio-polymer or a combination thereof. In certain specific embodiments, wherein the matrix powder is a bio-polymer, the bio-polymer is chitosan.

[0009] In embodiments of the invention concerning the milling process, in certain embodiments, the milling process is between 2 and 10 hours and the milled product comprises graphitic and amorphous carbon. In such embodiments, the milled product comprises less than 15% by weight of sp³ bonded carbon species after milling.

[0010] In still further embodiments of the invention concerning the milling process, the milling process is between 0 and 2 hours and the milled product comprises graphenes and graphitic carbon less than percentage 8 % by weight of sp³ bonded carbon after milling.

[0011] In other embodiments of the invention concerning the milling process, the process is greater than 10 hours and less than 50 hours. In such embodiments, the milled product comprises nanodiamonds. In such embodiments, the milled product comprises greater than 15% by weight of sp³ bonded carbon species after milling.

[0012] In still further embodiments concerning the milling, ethanol is added to the fullerene soot during the milling process. In such embodiments, the milled product has a larger surface area with which to interact with the one or matrix powder. In certain embodiments, the milled product possesses a surface area of approximately 270 m²/g or greater.

[0013] In greater specificity, in certain embodiments, when combining the at least one matrix powder, this step is accomplished while the soot is being subjected to mechanical milling. In other embodiments, the milled product is combined with the one or more matrix powder and subjected to a second milling as an alternative.

[0014] In certain further embodiments, the method disclosed herein further comprises sintering after the step of combining the milled product with at least one matrix powder to generate the carbon nano-reinforcement material.

[0015] In another embodiment, the invention concerns a reinforced polymer matrix, the polymer matrix made by combining carbon soot with a liquid polymer matrix to form a complex and hardening the complex to form a reinforced structure.

[0016] In certain aspects of the aforementioned embodiment, at least 90 % of the carbon soot is sp² bonded in the reinforced polymer matrix. In certain further aspects concerning the soot, the density of the carbon soot is about 0.2 to 2 g/cm³.

[0017] In embodiments of the aforementioned invention, the reinforced structure comprises 1% by weight of soot. In such embodiments, the reinforced structure has properties different than a hardened polymer structure that has not been reinforced with soot. For example, in certain embodiments, the addition of soot increases the tensile strength. In other aspects, wherein the reinforced structure comprises 0.2% by weight of soot, the addition of the soot increases the plasticity at least by 10%. Still further, the soot increases the average elastic modulus by at least 15% over the hardened polymer structure that has not been reinforced with soot; and increases the hardness by at least 20%.

[0018] In other embodiments of the invention, the reinforced structure comprises 3% by weight of soot. In such embodiments, the addition of the soot increases the plasticity at least by 6% over a hardened polymer structure that has not been reinforced with soot. Still further, the soot increases the average elastic modulus by at least 8% over the hardened polymer structure that has not been reinforced with soot; and increases the hardness by at least 10%.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] In order that the manner in which the above-recited and other enhancements and objects of the invention are obtained, we briefly describe a more particular description of the invention rendered by reference to specific embodiments thereof which are illustrated in the appended drawings. Understanding that these drawings depict only typical embodiments of the invention and are therefore not to be considered limiting of its scope, we herein describe the invention with additional specificity and detail through the use of the accompanying drawings.

[0020] Figure 1. Characterization of the soot in the raw and milled conditions by means of (a) Raman and (b) XRD. Note: the milling times for (b) the XRD are 2 hours and illustrate that milling media (steel vs zirconia) have a direct effect on the characteristics of the produced carbon nanostructures. Therefore, milling time changes depending on the milling media. Steel in this case synthesizes the graphene and graphitic carbon faster than zirconia.

[0021] Figure 2. High resolution electron transmission microscopy (HRTEM) of the (a) raw soot and (b-d) milled soot. In (b) is observed a graphitic particle responsible for the reflections identified in the Fast Fourier Transformation (FFT) pattern in the insert (see arrows and dotted circles). (c) The Inverse FFT of the identified reflection clearly reveals the presence of the graphitic structures in the investigated powder and the corresponding d-spacing analysis is presented in (d) with a value of 0.335 nm.

[0022] Figure 3. (Left) French-press and custom designed heater system used to sinter chitosan and chitosan-milled soot samples (Center) heater and die demonstrated in pictorial form. (Right) PC-based-DAQ thermal analysis system.

[0023] Figure 4. Characterization of the raw (a,c) chitosan and (b-c) soot by means of (a,b) scanning electron microscopy, and (c) X-ray diffraction.

[0024] Figure 5. (a) Heating/cooling curve for chitosan and (b) the first derivative of the heating/cooling curve. Samples of chitosan before (c-left) and after (c-right) the degradation temperature.

[0025] Figure 6. XRD results of sintered chitosan and chitosan-milled soot composites sintered at (a) 180 °C and (b) 220 °C. CI% stands for the crystallinity index. All samples were sintered for three hours except for the raw chitosan that was only pressed during sintering and a sample that was sintered for 12 h. In graph key for Figure 6a shows intensity levels from top to bottom, with top being 30h + milled soot and bottom being 6h. In graph key for Figure 6b shows intensity levels from top to bottom.

[0026] Figure 7. Raman analysis of the chitosan and chitosan-milled soot composites. Notice the significant differences in the Raman spectra at the different magnifications used in the present work. Note: the following samples were observed at 100 X: chitosan, sinter chitosan and composite powder; while a 1000 X magnification was used for the composites (sintered and powder).

[0027] Figure 8. Scanning electron micrographs of the (a) chitosan powders (b) the chitosan-milled soot composite milled for 6 h. Sintered samples at 180 °C of (c) chitosan, (d) chitosan-milled soot composite and (e) chitosan-milled soot composite sintered at 220 °C. Note: the diameter of the sintered samples is 25.4 mm. HRTEM images are presented in (f,g); micrograph in (g) corresponds to the encircled area in (f) at higher magnification to depict the graphitic nature of the milled soot having a d-spacing of 0.34 nm.

[0028] Figure 9. Optical characterization of the (a,b,c) chitosan samples and (d,e,f) chitosan-milled soot composites. Sample (a) was compacted at room temperature, samples (b-f) are the sintered samples. The sintered samples at 180 °C are (b,d,e) and the samples sintered at 220 °C are (c,f). All micrographs correspond to a sintering under a constant pressure of 3.5 MPa for 3 h. Arrows are used to indicate the gaps along the grain boundary.

[0029] Figure 10. Nanohardness results for the chitosan and chitosan-milled soot composites milled for 6 h, and sintered for 3 h at 220 °C. The insets are tapping mode images from the nanoindenter, in the chitosan samples the dotted circles are used to identify the Berkovich impressions. Note: the Berkovich impressions in the chitosan-milled soot composite were not identified. Demonstrating the high resistant to permanent damage of the carbon nanostructures and an unprecedented elastic behavior in the composite.

[0030] Figure 11. Characterization of SPS samples by means of (a) Raman spectroscopy, (b) TEM dark field mode, and (c) confocal image of a microhardness indentation. The arrows in (b) point towards the direction of deep scratches made with the ion mill during samples preparation. The particles (encircled) show no damage demonstrating its high hardness that it is attributed to its diamond nature. The bright particles in (c) are presumably micro diamonds found in the sintered samples.

[0031] Figure 12. Characterization of soot by means of: (a) SEM, (b) HRTEM, (c) XRD, (d) Raman and (e) TGA. In (d) the C60 – Ag(2) refers to a Raman band of fullerene (C60). The inset in (b) is a magnified region of one of the soot particles.

[0032] Figure 13. SEM micrographs of (a) epoxy and composites with (b) 1 wt% soot, (c) 3 wt% soot and (d) Raman results of the epoxy and composites.

[0033] Figure 14. Tensile testing results of the epoxy and the composites with 1 wt% and 3 wt% carbon.

[0034] Figure 15. SEM micrographs showing the effects of carbon soot particles on the epoxy-soot composite containing (a, c) 1wt% soot and (b) 3wt% soot. The arrow indicates the direction of the applied stress along.

[0035] Figure 16 Micrographs of the parallel nanoscratch test results on (a) epoxy, and composites with (b) 1 wt%C, (c) 3 wt%C and (d) lateral forces during nanoscratch test using a Knoop tip with loads between 5 to 9 mN with 1 mN increments at 30 μ m intervals.

[0036] Figure 17. Variations of friction coefficient as a function of applied normal load for the epoxy and the composites with 1 and 3 wt % soot.

[0037] Figure 18. Results of (a) modulus and (b) nanohardness for the epoxy and composites with 1 and 3 wt% soot. The scales at about 155 nm indicate the average values and the standard deviation for hardness and modulus respectively. The inset shows micrographs revealing the sample's surface before and after indentation, the red circles identify indentations.

DETAILED DESCRIPTION

[0038] In the embodiments of the invention disclosed herein, a methodology has been identified to produce nanostructured carbon particles that act as effective reinforcements.

[0039] In certain embodiments, the process is conducted in the solid state at close to ambient conditions. The carbon nanostructures produced under this embodiment are nanostructured and are synthesized by mechanical means. The milling is carried at room temperature. More specifically, the reinforcements consists of graphene, graphitic carbon and nano diamonds that are synthesized in situ during mechanical milling and then subjected to sintering to further enhance their effectiveness as reinforcement improving the intimacy with the carbon matrix.

[0040] The benefit of this processing methodology is that those carbon nanostructures behave as effective reinforcements when added to different matrix and sintered. This demonstrates its effectiveness in a wide variety of matrices including, but not limited to: ceramic, metallic, and polymeric (organic and inorganic), as well as bio-polymers. The reinforcements have been introduced in those matrices at room at elevated temperatures. The raw material is carbon soot that is a byproduct and hence abundant and cheaper than pristine carbon alternatives (e.g. nanotubes, graphene).

[0041] In standard practice, carbon nano-reinforcements are usually produced by evaporation (e.g. fullerene, nanotubes, graphenes, etc.) the processing methods are costly and in some cases

toxic. In addition, the processing techniques do not allow production of more than fractions of a gram per hour.

[0042] In the embodiments of the invention disclosed herein, abundant carbon nanostructures are produced mechanically. In such embodiments, the several grams to kilograms of the carbon nanostructures are produced per hour. In still further embodiments, the mechanically produced carbon nanostructures can be scaled up such that the carbon nanostructures can be produced on the mega-gram scale per hour. In such embodiments, scale up entails increasing the amount of fullerene soot, increasing the number of milling apparatuses, increasing the size of the milling apparatuses, increasing the surface area of the soot to the milling process, or some combination thereof.

[0043] In certain embodiments, the aforementioned mechanically produced carbon nanostructures are used as filler. More specifically, they are employed as filler for composites which allows the carbon nanostructures to complete their physicochemical interactions during processing. In certain embodiments wherein the carbon nanostructures are fillers, the carbon nanostructures behave as effective reinforcements and are effective in a wide variety of matrices including, but not limited to: ceramic, metallic, polymeric (organic and inorganic), as well as bio-polymers.

[0044] The processing can be conducted at room or elevated temperatures. For example, at room temperature this material has been tested using polymeric matrices and at elevated temperature we have used metals, ceramics, inorganic polymers (carbon), and bio-polymers (chitosan). Other carbon reinforcements (fullerene, nanotubes, graphene, fibers. etc.) have never demonstrated such level of effectiveness.

[0045] The embodiments of the invention disclosed herein not only reduce cost, but also facilitate direct implementation at the industrial level with minor modifications. In application, the manufacturing is non-toxic as compared to other carbon nanostructures that required toxic procedures.

[0046] In prior applications the use of other nano-reinforcements required sophisticated equipment for synthesis. Additionally, with the requirement that the manufacturing process should prevent physical damage to the reinforcement, the mechanical and the general physical properties of the other carbon nano-reinforcements are only preserved as long as the integrity of

the reinforcement is not compromised. This limits the manufacturing methods that can be used to industrialize or commercialize the final products.

[0047] The embodiment disclosed herein allow for integration of the reinforcement into the matrix with currently available technologies. In our case, the proposed reinforcement can be integrated into the matrix with currently available technologies. We identify that this reinforcement does not require special processing techniques to be used.

[0048] The invention disclosed herein can have variable amounts of graphitic and diamond or diamond-like carbon structures. Both, the graphitic and diamond structures act as reinforcements that improve the strength of the matrices where they are added. The processing methodology that we follow is comprised of mechanical milling of the commercial soot. During short time milling the soot agglomerates by welding which are needed as pre-conditioning state to form the carbon nanoreinforcements.

[0049] The agglomeration sponsors the synthesis of graphene-like particles. Results indicate that milled soot follows this sequence as a function of time: a) 0-5 h amorphous carbon, graphene and graphitic carbon, b) 5-10 h amorphous carbon, graphitic carbon and nano-diamonds (less than 15 percent by weight sp³ bonds), c) 10 + h amorphous carbon, graphitic carbon and nanodiamonds (less than 15 percent by weight sp³ bonds). However, this is quite dependable of the milling media (e.g. using a high energy SPEX mill, steel vials and milling media). Further, as the milling time increases, the contamination from the milling media may increase. Those times change for ceramic and for tungsten carbide milling media. Further, this can be escalated to an industrial set up, and the times can be adjusted then.

[0050] The graphene, graphitic carbon and the diamond are of interest for the reinforcements because they play different roles. The graphene and graphitic carbon have the largest aspect ratio; therefore, they are more efficient to coat the matrix particles. In certain embodiments transition metals are added to the blend as catalyst. Those metals act as hetero-nuclei to synthesize nanotubes and nanofibers during sintering. The nano-diamonds act as locally to harden the composite.

[0051] In certain embodiments, the production of milled powders with catalysts in the amount of 1-50 wt% (iron, nickel, or copper) are employed. Chemical reactions among the catalyst and carbon must be prevented; hence, milling time as well as sintering time and temperature is critical. In certain embodiments, the excessive agglomeration of the carbon particles is prevented

by adding a control agent (e.g. ethanol) during milling; after milling the particles can be dispersed by sonication in liquid media. Keeping the powder loose is important because the larger the surface area the better the reinforcement will be to coat the matrix particles. In certain embodiments, the surface area of the milled particles can be up to 270 m² /g.

[0052] In certain further embodiments, milled and/or sonicated powders are used directly in suspension by adding the matrix powders to the suspension followed by a second sonication. In other embodiments, the powders are dried out and milled again to generate the coating along the matrix particles. In certain embodiments, sonication is conducted in alcohol to disperse the powders to increase their surface area. The dried powders can be added to a second milling with the matrix of the particles to guarantee their integration. Examples of dried powders include: metals, ceramics, glasses, inorganic polymers (carbon), bio-polymers (e.g. chitosan), etc. The carbon powders are engineered to resist mechanical milling, which as of today has not been possible with other types of carbon (e.g. nanotubes or graphene). In the case of organic polymers (e.g. epoxies) the powder can be added directly to the liquids and mixed them thoroughly until they are integrated and homogeneously distributed within the liquid. The milled powders can then be sintered or the organic polymers can be allowed to set.

[0053] In certain embodiments, the reinforcement additions will vary from 1 to 20 wt%. In embodiments, wherein organic polymers are used, we have added up to 13 wt% with positive results.

EXAMPLES

[0054] The following examples are included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventors to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit or scope of the invention. The following Examples are offered by way of illustration and not by way of limitation.

[0055] Example 1: Characterization of All Carbon Composites Reinforced with In situ Synthesized Carbon Nanostructures

[0056] Materials and Methods

[0057] The purchased fullerene soot is produced by the Kratschmer method having traces (less than 1 wt%) of fullerene. The fullerene soot is the byproduct obtained after the purification of fullerene.

[0058] Methods

[0059] Mechanical milling is carried on the soot using a SPEX mill and steel hardened media for times from 0-50 h. After mechanical milling the powders are sonicated on a Misonix 4000 apparatus operated at 10-50 W for 2-30 min. The spark plasma sintering (SPS) conditions have been: temperature 1500 °C, 60 s, and heating rate of 140 ° C/s and a constant pressure of 100 MPa. The average dimensions of the sintered samples are 12 mm in diameter and 3 mm in thickness. The nanohardness apparatus is a Hysitron TI-900 TriboIndenter™ system that provides real-time data collection. A series of 9 measurements are made in an array allowing 15µm each side among indentation using 7000 µN.

[0060] The X-ray diffraction (XRD) is carried on a D5000 SIEMENS diffractometer, with a characteristic $\lambda^{\text{CuK}\alpha} = 0.15406$ nm operated at 40 kV and 30 A. The Scanning Electron Microscopy (SEM) observations are carried out on a FEI XL-30FEG on secondary electrons. The transmission electron microscope (TEM/HRTEM) for the raw soot is conducted on a JEOL JEM200FXII and atomic resolution is conducted in the TEAM 05 microscope from the Lawrence National Laboratory. The Raman characterization is done on a confocal micro-Raman microscope XploRA™, Horiba JY. The lasers used for the Raman excitation include the following wave lengths: 532 nm. The x-ray photoelectron spectroscopy (XPS) is conducted on a Physical Electronics XPS Instrument Model 5700. The XPS is operated via monochromatic Al-K α X-ray source (1486.6 eV) at 350 W.

[0061] Results

[0062] Figure 1 shows the Raman characterization of the raw and milled powders and the Raman lines for D, G and 2D bands of graphitic (sp²) carbon located at 1318 cm⁻¹, 1578 cm⁻¹, and 2660 cm⁻¹, respectively. The Raman spectrum shows that the 2D and D bands change with milling time. Short milling times are ideal to synthesize relatively large graphene or graphitic carbon. We estimated that the average lateral size of graphitic particles varies from $L_a \sim 40$ to 70 nm using the expression: $L_a(\text{nm}) = (2.4 \times 10^{-10} \cdot \lambda_{\text{las}}^4) (I_G/I_D)$, where $L_{\text{las}} = 532$ nm is the excitation laser wavelength, and I_G and I_D are the Raman intensity of the D and G bands, respectively [19].

The XRD reflections (111), (200), and (220) are characteristic of fullerene, a mix of C₆₀ and C₇₀. Further, fullerene is identified by Raman and XRD, but its presence is in amounts of less than 1 wt%. The milled powders show a development of ordered structures as a function of milling time; though, this also depends on the milling media. In the early stages of milling the quasi-amorphous carbon agglomerate forming double and triple graphene layers. The increase in the ratio D/2D bands indicates the presence of graphene and graphitic carbon.

[0063] Figure 2 shows images of the milled and raw soot. Both samples are analyzed by means of HRTEM. The raw sample is clearly amorphous and any short range ordered structures are attributed to the presence of bezoic-like rings as seen in the XRD patter. After the milling the samples develop larger range ordered structures with graphitic structures that are identified in Figure 2. In the milled powders the presence of graphitic particles is evident with interplanar distances (d-spacing) from 0.334 to 0.373 nm. The actual d-spacing for graphitic carbon is approximately 0.335 nm the reported differences herein are attributed to residual stresses. The residual stresses are the result of excessive bending among the particles. Those graphitic structures are the main contributors to effective reinforcement for composites.

[0064] The XPS results of the raw and milled material provide evidence that the amount of sp³ bonding increases with milling time up to 20 h; after that it decreases. This is in agreement with Raman. The drop in sp³ bonding at milling times of more than 20 h is due to chemical reactions with Fe that is contamination from the milling media. The Fe contamination increases with the presence of diamond forcing chemical reactions among the components that produce Fe₃C. The sp³ bonding is in part due to the presence of diamonds; however, some sp³ bonding is due to dangling bonds on carbon. The rest of the carbon (sp²) is a mix of amorphous, graphene and graphitic carbon. In the present work the emphasis is on the graphitic particles because they induce novel mechanisms with unique elastic characteristics.

[0065] Table 1 shows the XPS results of the milled samples at various times. The presence of iron (Fe) is the result of contamination due to the milling media. The oxygen present in the sample is identified forming various carbon species such as: C-O-H, C=O, CHn, C=O.

Table 1		
Milling Time	Elements	Carbon Species

(h)	C (at%)	O (at%)	Fe (at%)	Sp2 wt%	Sp3 wt%
0	94	6	0	95.75	4.25
0.5	90.7	9.3	0	87.99	12.01
2	88.43	11.57	0	87.07	12.93
10	83.27	16.25	0.48	84.2	15.8
20	83.87	15/5	0.63	81.75	18.25
50	87.3	12.7	3.31	91.25	8.72

[0066] Sintered Composites

[0067] The sintering conditions are selected to preserve the nanostructured nature of the composites while achieving high density. The densities in the sintered samples vary depending on the milling conditions and sonication; though, in all the cases the density is above 2 g/cm^3 that is comparable to that observed in graphite ($2.09\text{-}2.23 \text{ g/cm}^3$).

[0068] The characterization of the sintered sample is presented in Figure 11. In this figure are presented Raman, TEM and a confocal image of the microhardness testing results. The Raman spectrum shows two main characteristics: i) the first is the intensity of the 2D band clearly demonstrating the presence of the graphitic structures at short milling times, likely graphene and ii) the position of the D band that is similar to that reported for diamond (1334 cm^{-1}) [25], at larger milling times. The presence of diamond is further confirmed by the dark field images in Figure 4b. In Figure 4c the diamonds are observed as translucent crystals when under the optical microscope in confocal mode. The dark field image presents “scratches” (indicated by an arrow) along the sample. The scratches result from the ion milling device preparation. The ion mill scratches show clear cuts through the carbon matrix (blend of amorphous and graphitic carbon); though, it does not incur any visible damage onto the “bright” particles. This is a clear demonstration of the high hardness of those particles that are presumably identified as diamonds. The differences in mechanical properties among the graphitic and amorphous carbon structures and diamond may be responsible for the fracture presented in Figure 11c. This fracture occurred during microhardness testing. The fracture shows the internal microstructure of the sintered samples exposing a large density of translucent crystals presumably microdiamonds.

[0069] Summary

[0070] In the mechanical milling of fullerene soot phases such as graphitic carbon and diamond can be synthesized. Short milling times are recommended to synthesize graphitic carbon (likely sp²). Larger milling times are more effective to increase the presence of sp³ bonding. The Sp³ bonding is attributed to diamond and dangling bonds in the thermomechanically processed samples. The presence of graphitic carbon and diamond were successfully characterized by means of XRD, Raman and TEM. Through a systematic material characterization we identify a novel manufacturing route to for carbon reinforcements produced in situ in a carbon matrix. The mechanical effects to synthesize graphitic carbon and diamond are further enhanced during SPS.

[0071] Example 2: Chitosan and Chitosan Composites Reinforced with Carbon Nanostructures**[0072] Methods**

[0073] Samples were prepared using 80 % deacetylated chitosan (Carbomer Inc, San Diego CA) and commercially available fullerene soot (SES Research, Houston TX). Mechanical milling was conducted on a SPEX apparatus for 6 and 30 h for the chitosan and 0.5-3 h for the fullerene soot. The chitosan-milled soot composite samples were mixed at a 98:2 weight ratio (chitosan-milled soot) and milled together for an additional 1.5 h. The sintering was performed on a custom made French press-heater (Figure 3).

[0074] The temperature was monitored via high speed, high resolution data acquisition system (NIcDAQ-9174; National Instruments, Austin TX) as shown in Figure 3. The same system was used to collect the data for thermal analysis, but this process was carried in a tube furnace. The sintering was conducted at 180 and 220 °C for 3 and 12 h under a constant pressure of 3.5 MPa through the entire sintering process. All experiments were carried out in a helium atmosphere. The temperature during sintering was measured in close proximity to the die (see Figure 1). Through calibration of the equipment, we determined that the sintering temperature can be up to 30 °C lower to that measured by the thermocouple. We used this temperature to offset the collected data.

[0075] Hardness testing was performed on all samples using micro and nanohardness methods. For microhardness we used the Vickers method on a M-400-G Lecco apparatus with a load of 150 g-f and dwelling time of 10 s. The nanohardness was performed in a Hysitron TI-900

TriboIndenter™ system with real-time data collection. The reported values are the average of 6 measurements. The applied load was 1000 μN . The system has a 1 nN and 0.0004 nm resolution in loading and displacement respectively. X-ray diffraction (XRD) was measured with a D5000 SIEMENS diffractometer at $K\alpha = 0.15406 \text{ nm}$. The crystallinity index is determined based on the expression: $\text{CI}\% = [(I_{110} - I_{\text{am}})/I_{110}] * 100$ where CI% is the crystallinity index, I_{110} the intensity (arbitrary units) of the reflection (110) for the β -phase and I_{am} the intensity of the amorphous phase (α) [14, 15]. The presence of the γ -phase is not possible by the use of a similar XRD expression. The SEM observations were carried out on a FEI XL-30FEG on secondary electrons. Finally, a Raman analysis was done on a confocal micro-Raman microscope XploRA™, Horiba JY. A 638 nm diode laser was used for excitation.

[0076] Results

[0077] SEM and XRD characterization of the raw materials are shown in Figure 2. The SEM image of chitosan shows a chunky structure with a regular distribution of particles of various sizes. The XRD results indicate that chitosan has a defined crystalline structure. The XRD results suggest that chitosan is composed of both, α and β , phases with a crystallinity index of 57. The fullerene soot is characterized by the fluffy appearance (Figure 4c). Figure 4b shows the presence of fullerene and a short range ordered phase (identified as $(002)_{\text{Gr}}$), characteristic of the basal plane of graphite. The fullerene soot is the byproduct, leftover, after the recovery of fullerene produced by the Kratschmer method. Fullerene is expected since the soot is the byproduct after the fullerene removed. The supplier indicates that fullerene is present on traces and no more than 1wt% is present in the soot that is in agreement with the observations.

[0078] Figure 4d shows an integrated Raman spectrum of the fullerene soot with bands of C_{60} ; one fundamental and one second-order combinational identified at 710 cm^{-1} ($\text{Hg}(3)$) and at 2898 cm^{-1} ($\text{A}_g(2) + \text{H}_g(7)$), respectively. The other Raman bands of C_{60} are weaker and they may be hidden under the G and D bands of graphitic carbon. The main Raman bands are D, G and 2D bands of graphitic (sp^2) carbon at 1318 cm^{-1} , 1578 cm^{-1} , and 2660 cm^{-1} , respectively. Graphitic carbon may also contribute to the band at 2898 cm^{-1} through the D+G two-phonon scattering channel. The estimated average lateral size of graphitic particles is 40 nm.

[0079] Figure 5 shows the heating/cooling and first derivative of temperature with respect to time for the raw chitosan (80% deacetylation). The heating/cooling curve demonstrates the presence of phase transformations. The optimal sintering temperature is near, but below the

degradation temperature. Temperatures above degradation damage the chitosan permanently with negative consequences for sintering. This deterioration is observed in Figure 5b by the exothermic reaction (likely burning) taking place above 215 °C and it is confirmed by the discoloring ashy appearance of the loose material. Based on the collected information we used the criteria that sintering temperature (T_s) should be conducted at $T_s = (0.8-0.9) \cdot T_T$, where T_T is the transformation (in this case degradation) temperature in K. These conditions were set to guarantee that the minimum activation energy requirement for sintering are met at temperatures below degradation to reduce sintering time. The approximate weight loss in the sample seen in Figure 5c,d are 12 and 30 wt% in weight respectively.

[0080] The XRD results are presented in Figure 6 for the sintered samples at 180 °C and 220 °C. Both figures demonstrate that milling time lowers the crystallinity index. It is also interesting to see that the presence of milled soot slightly reduced the CI%. The major contributor to the reduction of the CI% seems to be the sintering time. This effect is observed by the enhancement of the α phase of chitosan that is also known as the amorphous phase. The samples milled for 6 h have comparable CI% except for that one sintered for 12 h that has the lowest CI% of 20 suggesting that sintering time has a more a negative effect on crystallinity than milling time.

[0081] Raman characterization was conducted to observe the effects of milling and sintering on chitosan and to show the effects of carbon nanostructures on the composites in powdered and sintered forms. The analysis conducted in bulk (100X magnification) on the powders, sintered chitosan and sintered chitosan-milled soot composite are almost identical (Figure 7). At this magnification Raman active bands in the powder as well as the composites before and after sintering can be identified. At 1087 cm^{-1} the skeletal vibration C-O stretching generally related to the saccharide structure typical of chitosan. The anti-symmetric C-O-C bridge is the band observed at 1154 cm^{-1} and it is indicated with a B. The identification of the Raman bands correspond to the C-H bending at approximately 1381 and 1423 cm^{-1} and are identified as C and E in Figure 7 respectively. The N-H bending mode is typically found at 1598 cm^{-1} and corresponds to the primary amine group (letter F).

[0082] From Figure 7 it is evident that magnification makes a difference in the Raman analysis. Using a magnification of 1000 X the Raman analysis goes from bulk to discrete allowing a clear identification of the carbon in the chitosan-milled soot composite. Fullerene is not identified by Raman in the composite because its presence is in parts per millions

compromising its identification. The carbon milled soot are identified by the G and D bands. These are the two most common bands of carbon. The G band is also called the graphite band and related to graphitic bonding (sp^2). The D band is the defect band that is usually active in nanostructured graphitic particles. Due to the relative intensity among the D and the G bands it can be concluded that the carbon used in this work has a graphitic nature with a high density of defects. The D band should not be confused with the diamond band that is a narrow and sharp at 1334 cm^{-1} . The magnification demonstrate that the carbon nanostructures are located at the surface of the chitosan as coating promoting superior sintering of the composite.

[0083] Figure 8a-b shows micrographs of the powders before and after milling. The powder before milling is composed of particles of approximately $50\text{ }\mu\text{m}$ or larger. After milling the powders agglomerate into clusters that are carbon coated along their surface. Pictures of the sintered samples are given in Figure 8c-e. The change in color in the composites is attributed to the carbon additions. The chitosan has an off-white color while sintering results in a browning of the material. The chitosan-milled soot composites are highly homogeneous as shown by their consistent dark color at only 2 wt% of added milled soot. HRTEM images of the milled soot are presented in Figure 8f-g. Those figures show that the CNS have graphitic nature with interatomic distance of 0.34 nm similar to that on graphene. The crystal size of the graphitic particles is about 40 nm as calculated in our previous work.

[0084] Figure 9 shows optical micrographs of chitosan and chitosan-CNS composites. In Figure 7a the compacted chitosan and Figure 9d the chitosan-CNS composite sintered at $180\text{ }^\circ\text{C}$. In the chitosan samples the grain boundaries are wider than those in the sintered samples. This results from the expected low cohesion among the chitosan particles that is improved with the sintering conditions and CNS additions. The grain boundaries in the chitosan-CNS composite are relatively difficult to identify; although, some porosity is still present, but in lower amounts and smaller sizes. In the higher magnification images, it is possible to visualize the grain boundary and the effect of temperature and carbon in the chitosan-CNS composite. The arrows in Figures 9c-f are used to indicate the grain boundary. In the chitosan sintered samples, this gap is $2\text{-}4\text{ }\mu\text{m}$ range. In the case of the chitosan-CNS composite the gaps is sub-micrometric (1-2 orders of magnitude smaller).

[0085] Table 2 summarizes the microhardness testing results of the chitosan and the chitosan-CNS composites. The chitosan samples show the lowest hardness in particular when they are

sintered at 180°C. When the chitosan samples are sintered to 220 °C the hardness increases. The samples were sintered using a 3.5 MPa of constant loading. However larger milling times (30 h) seem to have a negative effect on hardness. The contrary is observed with the addition of CNS. A direct comparison among the hardness in the chitosan sintered samples with that in the composites show improvements of 14-15 % for the samples sintered at 180 °C and only 13% difference when sintered at 220 °C. Sintering for 12 h compared to 3 h does not seem to affect hardness. The consistency of the pressed sample without sintering is so delicate and weak that hardness measurements were not possible. Therefore if we compared the results with that sample we can conclude that the composite has appreciably higher mechanical properties.

Table 2

Table 2			
		Microhardness (μHV)	
Sample	Milling Time	180°C	220°C
Chitosan	6h	18.4±5.4	23.1 ± 1.6
Chitosan	30h	15.1±0.7	23.6 ± 0.1
Chitosan-CNS Composite	6h	21.2±2.5	26.1 ± 2.7
Chitosan-CNS Composite	30h	17.6±1.8	24.1 ± 0.6
			26.2 ± 0.8*
*Sample sintered for 12h			

[0086] Figure 10 shows the results of nanohardness for the chitosan and chitosan-CNS composites. The respective hardness values are 265 and 287 MPa that represent an 8 % improvement. The elastic moduli are 7.0 and 2.1 GPa that correspond to a 73 % increase in the chitosan sample. The recovery for the chitosan is 42 % while the recovery for the composite is 72 %. This recovery and elastic deformation observed in the composite is unique and is directly attributed to the additions of CNS. The nanohardness indentations were resolved by the scanning system in the chitosan, but were not observed in the chitosan composite. This phenomenon is attributed to the elastic behavior resulting from the CNS that allows for a better recovery of the composite. The grain boundary in the chitosan sample is larger than that of the composite confirming the results presented in Figure 9.

[0087] Discussion

[0088] Thermal analysis is an effective method to control the phase transformations occurring during the heating of chitosan. These phase transformations have distinct heat transfer characteristics as indicated by the change in slope of the heating/cooling curves. The first derivative of temperature with respect to time vs. temperature not only determines the transformations but the level of reversibility of the sample as well. The algorithms reported in were designed to determine the fraction of the material that is changing phase or “fraction transforming”. Heating an organic material above the degradation temperature decomposes it; such phenomenon is presented in Figure 3a-b. The irreversibility, in this case, is attributed to the burning of chitosan. Therefore, proper sintering of chitosan must be conducted at temperatures close, but below, that when chitosan starts degrades.

[0089] Comparing Figure 3-5 it can be observed that after the degradation temperature chitosan transforms to ashes. On the other hand mechanical milling affects the crystallinity of chitosan as seen from the XRD results. This does not imply that the bonding structure is affected; in fact, the Raman results of before and after the milling are identical. Nonetheless, the microhardness of the samples is negatively affected up to 20%.

[0090] Mechanical milling is an effective method to refine the grain structure of chisotsan and it helps to develop an even distribution of particle sizes. Additionally, it allows the proper formation of a composite by dispersing the CNS homogeneously. This can be confirmed by the uniform change in coloration. This in turn allows a better sintering potential as shown in Figure 6 and Figure 7 and further confirmed by the improvements in hardness shown in Table 1. The ultimate contributor to the integrity and consistency of the composite is the presence of CNS. However, at the nanoscale the composite does not seem to have significant improvements on hardness; nonetheless, the elastic characteristics of the composite improve significantly (Figure 8) allowing an almost full recovery of the material. Further, this prevents the proper observation of the nano-indentation. It is of interest that only 2 wt% of CNS is sufficient to have such improvements in mechanical properties. The elastic moduli, hardness, and recovery of the composite presented herein are superior to those previously reported in composites reinforced with nanotubes and uncrossed-linked chitosan. We attribute this elastic behavior to the graphitic nature observed in the milled soot as seen in Figure 5.

[0091] The single layer graphene had reported outstanding elastic behavior and self-healing mechanisms numerically and experimentally. Both mechanisms may be responsible for the elastic properties observed in the investigated composites. The graphitic nature of the milled soot used in this work was reported in our previous work, which in this work is observed in the XRD and Raman results presented herein.

[0092] **Example 3: Ultra-Ductile and Low Friction Epoxy Matrix Composites**

[0093] We present the results of an effective reinforcement of epoxy polymer matrix with fullerene carbon soot. The soot-epoxy composites show a remarkable increase in tensile elongation of more than 13 % in 1 wt% soot composite – an indication for a change of the failure mechanism in tension from brittle to ductile. Additionally, the coefficient of friction is reduced from 0.91 in plain epoxy to 0.15 in the 1 wt% soot composite. The lateral forces during nanoscratch decrease as much as 80 % with an enhancement of the elastic modulus and hardness by 43% and 94%, respectively. The epoxy composites containing 1 wt% of fullerene soot can be strong candidates for coating applications.

[0094] **Methods**

[0095] The fullerene soot is produced by the Kratschmer method and is the byproduct obtained after the purification of fullerene. The soot used in the present work has less than 1 wt% fullerenes (C₆₀ and C₇₀). Fullerenes are identified by XRD and Raman.

[0096] Resin (Epilox® T 19-36/700) is a commercially modified, colorless, low viscosity (650-750 mPa.s at 25 °C) epoxy resin with reduced crystallization tendency (density= 1.14 g/cm³). Its main components are Bisphenol A (30 - 60%), Crystalline silica (quartz) (1 – 10%), Glycidyl ether (1 – 10%), Inert fillers (10 –60 %). Hardener (H 10-31) is a liquid, colorless, low viscosity (400-600 mPa.s) modified cyclo-aliphatic polyamine epoxide adduct. Cross linker (Epilox® Hardener H 10-31) is a commercially modified colorless liquid, low viscosity (400-600 mPa at 25 °C). Both the hardener and the cross linker have a density of 1 g/cm³, having as main components the 3-aminomethyl-3, 5, 5-trimethyl-cyclohexylamine benzylalcohol and Benzyl alcohol.

[0097] Resin (T 19-36/700), cross linker and filler CS were thoroughly mixed in specific ratio with mechanical stirring (20,000 RPM for 2 minutes). A subsequent sonication step (ultrasonic frequency 37 KHz for 15 min) followed by degassing in vacuum were performed to make sure that all trapped bubbles were completely removed. Before the onset of polymerisation, the

polymer was set into the mould. Handling strength for these composite occurs in 24 hours and complete curing occurs in 5-7 days, both at 25 °C. For faster curing the moulds were kept in the oven at 90 °C for 1 hour or 70 °C for 4 hours. Samples were prepared with two different CS concentrations: 1 and 3 wt%.

[0098] X-ray diffraction (XRD) was carried out using a D5000 SIEMENS diffractometer, with a Cu tube and a characteristic $K_{\alpha} = 0.15406$ nm operated a 40kV and 30 A. The scanning electron microscopy (SEM) observations were carried out using two field emission SEM's. One is a FEI XL-30FEG and the other is a FE-SEM, Zeiss Supra 40 connected to an Energy dispersive X-ray spectroscopy (EDS-Oxford Inca Energy 450). The high resolution transmission electron microscope observations (HRTEM) were carried in a Jeol 2000FX, operated at 200 kV. All images were analyzed in Digital Micrograph 3.7.1 software. X-ray photoelectron spectroscopy (XPS) was conducted on a Physical Electronics XPS Instrument Model 5700, operated via monochromatic Al- K_{α} X-ray source (1486.6 eV) at 350 W. The data analysis was conducted on MultipakTM software and the Shirley background subtraction routine had been applied throughout.

[0099] The raw powder was analyzed before and after calorimetric analysis with Raman using a Renishaw Micro Raman system with green laser line (wavelength: 514 nm) equipped with a Charged-Coupled Device as a detector. The microscope used a 50X objective lens to focus the laser beam on sample surface, and the size of the focused laser spot on the sample has a diameter of a few micrometers. The composites were analyzed in a confocal micro-Raman XploRATM, Horiba JY using a Raman excitation green laser of a 532 nm at 1000X magnification.

[00100] For the characterization of mechanical properties, a defect-free region of the sample surface was selected by atomic force microscopy imaging prior the indentation test. Indentation measurements were conducted using a Ubi1 instrument (Hysitron, Minneapolis). The machine compliance and the area function of the tip were calibrated before the indentation test using a fused silica sample (ASMEC, Germany). The loading and unloading segments in trapezoidal three-segment load function were each completed over a time of 30 s irrespective of the maximal load (F_{max}). F_{max} was kept constant for 30 s. A reference sample of polycarbonate (ASMEC, Germany) was additionally measured to test the calibration condition of the device.

[00101] A set of 36 indents was carried out in a symmetric matrix spaced with a maximum load of 180 μN , where each indentation imprint is separated at least 4 μm to each other to avoid the influence of the stress fields around the indents and recording the load-penetration curve of each measurement. A 60 s delay at zero loads was established before and after each indent for thermal drift determination. The hardness is defined as $H_{IT} = F/A_c(h_c)$, where F is applied load and A_c is the contact area, which is itself function of the contact depth (h_c) as calculated by the Oliver and Pharr Method [Ref. W. C. Oliver and G. M. Pharr, "Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology," Journal of Materials Research, vol. 19, no. 01, pp. 3–20, Mar. 2003]. For the reduced elastic modulus, the following equation was used. See equation 1.

[00102] Equation 1:

$$[00103] \quad 1/E_r = 1-\nu_i^2/E_i + 1-\nu_s^2/E_s = (2/\sqrt{\pi})((\sqrt{A_c}(h_c))/S)$$

[00104] Where E and ν are the Young's modulus and Poisson's ratio and the subscripts, i and s associated to the indenter and sample, respectively. The contact stiffness, $S = dF/dh$ is estimated from the first part of the unloading segment of the load-penetration curve. It is worth to mention that the viscoelastic effects on the determination of reduced elastic modulus were neglected in this work but deserve to be determined in a separate contribution.

[00105] At least 5 nanoscratch tests were performed in each sample using a Knoop tip in an IBISUMIS nanoindentation device in a steady load mode and varying the load between 5 to 9 mN with 1 mN increments. Each scratch test was done over a length of 500 μm , recording continuously the lateral force as well as the friction coefficient through a force sensor LVDT. A pre-scan was done for slope correction, which is done with the closed loop PZT direct acting normal force sensor that keeps the load for curved or sloping surfaces.

[00106] Results

[00107] A summary of carbon soot characterization results is presented in Figure 12. The SEM micrograph in Figure 12 a reveals a fluffy morphology of carbon soot characterized by amorphous to short distance ordered carbon as well as nano-sized spherical carbon particles as seen in the HRTEM micrograph in Figure 12b. The main XRD results presented in Figure 12c are dominated by the (002) reflection of graphitic carbon and the x-ray signature of C_{60} fullertite particles. The Raman spectra in Figure 12d corroborate the XRD findings of graphitic structures with short lateral dimensions.

[00108] The TGA analysis demonstrates that the carbon is stable to temperatures of approximately 350 °C with a weight loss of less than 7 wt%. The weight loss of the carbon soot during the heating to 700 °C is another 83 wt%. We attribute the above weight reduction to the oxidation of the amorphous material first, followed by short-order graphitic structures. The remaining 10% was characterized by Raman showing comparable spectra to that seen in the raw material. We presume that this remaining carbon is nanostructured and the particles are graphite-like.

[00109] The carbon soot was analyzed by EDS and XPS, the results are presented in Table 3. Both methods found soot content comprising only carbon and oxygen in the soot. The XPS results show a majority of carbon and the balance is oxygen. Similar results were obtained with EDS confirming the findings. According to the XPS results up to 95.75 wt% of carbon is sp^2 bonded, whereas the remaining carbon forms sp^3 bonds. Lack of diamond traces in all analysis suggests that sp^3 bonds are dangling bonds and C-O groups along some of the edge atoms in the benzoic rings.

[00110] The Raman D and G bands shown in Figure 12d are typical for sp^2 rich carbon materials. The G band is due to the symmetric E_{2g} carbon vibrational mode, allowed by Raman selection rules, whereas the D band is a product of defect-induced Raman scattering involving carbon vacancies, functional carbon-oxygen groups, and boundaries of nano-sized graphite particles. The second-order Raman 2D and D+G bands involving two phonons appear only in sp^2 material with translational order. The BET results indicate that the surface area of the soot is 161 m^2/g and a density of 1 g/cm^3 . Concluding the soot is in the form of spheres composed of a mix of amorphous and graphitic structures with short range order and a high density of dangling bonds.

[00111] Table 3. Results of characterization of the soot by means of XPS, EDS and Raman. The grain size was calculated using the following model $L_a(nm) = 2.4 \times 10^{-10} L_{las}^4 (I_g/I_d)$ where where $L_{las} = 638$ nm is the excitation laser wavelength, and I_G and I_D are the Raman intensity of the D and G bands, respectively.

Table 3				
Elements		Carbon Species		Grain size

C	O	Sp2	Sp3	nm
(at%)	(at%)	wt%	wt%	
94	6	95.75	4.25	40

[00112] Figure 13 shows the SEM images of the epoxy and the composites with 1 and 3 wt% soot. The surface morphology of epoxy and the composites is markedly different; the latter reveals clearly the embedded spherical nanostructures (100-150 nm) in the polymeric matrix. Figure 13d shows that the epoxy Raman fingerprints are seen in the three investigated samples. The characteristic graphitic carbon band are clearly discernible and show little deviation from those observed in the raw soot (Figure 12d) indicating that no apparent damage or modification of the soot. Therefore, from those results we conclude that no chemical interaction between the epoxy and the soot takes place; instead, the interactions are through van der Waals forces. As expected, the intensity of the carbon response increases with the amount of soot.

[00113] The tensile testing results are presented in Figure 14. The epoxy sample shows a stress-strain curve characteristic for a brittle material with almost no ability for plastic deformation and an ultimate tensile strength (UTS) of 17.7 MPa. The measured epoxy Young's modulus is 1.8 GPa. The composite with 1 wt% of soot presents a slight increase of 5 % in UTS (18.6 MPa) whereas in that with 3 wt% soot the strength is comparable to that in the epoxy. The Young's modulus for both composites is approximately 2.04 GPa resulting in a 13.3% increase with respect to pure epoxy. The yield strengths are 13.2 and 12.3 MPa for 1 and 3 wt% soot additions respectively. The most important result, however, is the large increase of plasticity of the composites, particularly those reinforced with 1 wt% of soot reaching 13.2% elongation at a stress of 14.1 MPa. The composite with 3 wt% soot additions has a maximum elongation of 7.0 % at a stress of 14.3 MPa. These results suggest that the elongation of the epoxy composites can be tuned by varying the soot loading. Furthermore, both composites show upper and lower yield strengths similar to those observed in low carbon steels. In other words, the elastic behavior is the result of a work-hardening mechanism developed in the tensile testing.

[00114] Figure 15 shows SEM micrographs for the composites. The spherical soot nanoparticles are discernible in both composites. This figure also demonstrates the role of the spherical soot particles in the work-hardening effect in epoxy composites - the particles act as

anchors preventing the free crack grow. This mechanism is more effective in the composite with 1 wt% soot. Higher density of particles has a stress concentrator effect reducing the strengthening effectiveness of the soot. This is evident in the composite with 3 wt% soot. The strengthening mechanism is clearly depicted in Figure 15c where a particle dragged effect is observed and an extended crack propagation is tapped by the soot particles. In the presence of higher density of particles this effect is also evident, however, it is not as effective resulting the development of larger cracks and the detachment of larger sections of epoxy. The particle distribution observed in the 1wt% soot composite is more homogeneous and in the other composite the soot particles agglomerate. In both cases the strengthening mechanism is effective; nonetheless, agglomeration lowers the strengthening effectiveness of carbon soot.

[00115] Additions of different amount of soot to the epoxy matrix show remarkable effects on its tribological behavior. A summary of the nanoscratch testing results is presented in Figure 16, where the scratches along the surface on the investigated samples are clearly seen. The scratches were conducted using constant loads from 5 to 9 mN. Figure 16a, b and c correspond to the epoxy and the composites reinforced with 1 and 3 wt% soot, respectively. The load increases from the first to the last scratch as indicated in the figure and clearly evidenced by their thickness and depth. The deeper and more defined scratches are in the epoxy followed by the 3 wt% soot composite. This makes the 1 wt% soot composite the samples with less damage.

[00116] Figure 16d depicts the lateral forces during the nanoscratch test. A steady state is reached in all tests such that the forces are essentially constant. The 1 wt% soot composite has the least resistance to the nanoscratch. This is a consequence of a lubricity effect ongoing on this composite. The composite with 3 wt% soot present an increase in the lateral forces. Potentially, this results from the agglomeration of the soot spheres that may contribute to further interactions within the matrix resulting in a reinforcement effect of the composite. Furthermore, the epoxy is the sample presenting the highest lateral forces (Figure 16b-c). Besides the unprecedented plastic behavior in tension, the tribological properties of the composite present advantages over the epoxy. Those advantages include the decrease in lateral forces as well as the lubricity particularly in the 1wt% soot composite.

[00117] The results of measurement of the coefficient of friction as a function of applied normal load are presented in Figure 17. The friction coefficient in the 1wt% soot composite varies little with the test load, whereas for the epoxy and the 3 wt% soot composite the friction

coefficient decreases with loading. The respective reductions are from 0.91 to 0.59 when the load is increased from 5 to 9 mN. For the same condition in the case of the 3 wt% soot composite the values reduce from 0.56 to 0.39. The 1 wt% soot composite shows remarkable steadiness with a coefficient of friction consistently in the range 0.15 and 0.16. These demonstrates that the dispersion in epoxy of 1 wt% of soot leads to a decrease in the coefficient of friction up to 83% when using 5 μ N load and 73% with 9 μ N load.

[00118] The reduced elastic modulus and nanohardness results are presented in Figure 18. Again, particularly for the elastic modulus, viscous effects were not taken into account in this contribution. Based on a direct comparison, both properties are improved in the composites respective to the epoxy. The data scattering (standard deviation) in both composites is also reduced. This is an indication of the higher homogeneity in the material and effective reinforcement of the carbon soot. The composites show improvements in the average elastic modulus of 9.9 to 16.7% and the corresponding improvements in hardness are 16.6 and 28.6% for the composites containing 3 and 1 wt% soot, respectively. A further advantage in the composite is the clear reduction in the dispersion of the data demonstrating higher homogeneity and reinforcement. Considering the best and worst cases for reduced elastic modulus and hardness the improvements are: 49.8 and 93.5% respectively.

[00119] The use of fullerene soot to reinforce epoxy matrix result in an appreciable increase of ductility, friction and hardness. This particular type of soot is resistant to temperatures of up to 329 °C in air, which make it suitable for use in fire retardant applications. The presence and morphology of the fullerene soot in the composite is clearly identifiable by means of Raman and microscopy. During tensile testing the Young's modulus of the epoxy is preserved in the composite; therefore, we presume that the epoxy (matrix) does not suffer major molecular changes. This is also confirmed by the similarity in the Raman spectra in the epoxy when compared to those in the composites.

[00120] We relate the remarkable increase of elongation of the epoxy composites to the dragging effect of the soot particles. The combination of size of the spherical soot particles (<160 nm) and loading of 1 wt% result in an optimal homogeneous dispersion of large surface area particles within the epoxy (Figure 15). During the tensile tests, the stress is carried by the epoxy matrix until reaching the elastic limit. Further on, the carbon particles act as stress concentrators but because of their rigidity they start dragging. As a result both the dragging channels and

carbon particles become crack development stoppers. There is, however, a specific balance between particle size and particle concentration that makes the effect significant. Increasing the amount of soot addition results in unwanted agglomerations that reduce the reinforcement effectiveness.

[00121] During the scratch test, the lateral forces in the epoxy compared to those in the composites show marked differences. Larger lateral forces are observed in the epoxy while the lowest are found in the composite with 1 wt% soot having a force reduction of approximately 80%. We attribute that to a potential lubrication mechanism occurring in the composites while dragging the soot particles. In addition, the composite with 1 wt% carbon has the highest hardness and reduced elastic modulus with the narrowest the scatter of the data.

[00122] Conclusion

[00123] The additions of fullerene soot in epoxy demonstrate overall improvements in strength, hardness, coefficient of friction, and modulus of the resulting composites. The most distinguishable result, however, is the change in failure mechanisms from brittle to ductile during tensile testing. A remarkable increase of elongation is observed from 0.7% in the epoxy to more than 13% in the composite with 1 wt% soot. In the same composite the coefficient of friction is reduced by 83% along with an enhancement of modulus and hardness by up to 49% and 93.7%, respectively. These mechanical properties of the 1 wt% fullerene soot epoxy composite make it a very strong candidate for coating applications.

CLAIMS

1. A method of synthesizing carbon nano-reinforcement material, the method comprising:
 - a. obtaining fullerene soot with less than 10% by weight of fullerene; and
 - b. subjecting the soot to mechanical milling for between 0.5 and 50 hours to obtain a milled product; and
 - c. combining the milled product with at least one matrix to create a carbon nano-reinforcement material; and

wherein the at least one matrix is a metal, a ceramic, a glass, an inorganic polymer, a bio-polymer or a combination thereof

2. The method of claim 1, wherein the milling is between 0.5 and 5 hours.
3. The method of claim 2, wherein the milled product does not include nano-diamonds.
4. The method of claim 1, wherein the milling is greater than 5 hours.
5. The method of claim 4, wherein the milled product includes nano-diamonds.
6. The method of claim 1, wherein the milling is between 5 and 10 hours.
7. The method of claim 6, wherein the milled product comprises graphitic carbon.
8. The method of claim 6, wherein the milled product comprises less than 15% by weight of sp³ bonded carbon species after milling.
9. The method of claim 1, wherein the milling is greater than 10 hours and less than 50 hours.
10. The method of claim 9, wherein the milled product comprises less than 20% by weight of sp³ bonded carbon species after milling.

11. The method of claim 1, further comprising adding ethanol to the fullerene soot when subjecting the soot to mechanical milling.
12. The method of claim 1, wherein the milled product possesses a surface area of 270 m²/g or greater.
13. The method of claim 1, wherein the combining of the at least one matrix (i.e. polymer (epoxy), inorganic polymer (amorphous carbon), biopolymer (e.g. chitosan), ceramics, metals, among others with the milled product takes place when subjecting the soot to mechanical milling.
14. The method of claim 1, wherein the combining of the at least one matrix with the milled product takes place during a second milling of the at least one matrix.
15. The method of claim 1, wherein the carbon nano-reinforcement material comprises between 1-20 percent by weight of the milled product.
16. The method of claim 1, wherein the matrix is a bio-polymer.
17. A reinforced polymer matrix, the polymer matrix made by combining carbon soot with a liquid polymer matrix to form a complex and hardening the complex to form a reinforced structure.
18. The reinforced polymer matrix of claim 17, wherein at least 90 % of the carbon soot is sp² bonded.
19. The reinforced polymer matrix of claim 17, wherein the density of the carbon soot is about 0.2-2 g/cm³.
20. The reinforced polymer matrix of claim 18, wherein the reinforced structure comprises 0.2 to 1% by weight of soot.

21. The reinforced polymer matrix of claim 20, wherein the soot increases the tensile strength of the reinforced structure as compared to a hardened polymer structure that has not been reinforced with soot.
22. The reinforced polymer matrix of claim 21, wherein a measurement of Young's modulus is at least 10% greater than the hardened polymer structure that has not been reinforced with soot.
23. The reinforced polymer matrix of claim 21, wherein the soot increases the plasticity at least 10% greater than the hardened polymer structure that has not been reinforced with soot.
24. The reinforced polymer matrix of claim 21, wherein the soot increases the average elastic modulus by at least 15% over the hardened polymer structure that has not been reinforced with soot.
25. The reinforced polymer matrix of claim 21, wherein the soot increases the hardness by at least 20% over the hardened polymer structure that has not been reinforced with soot.
26. The reinforced polymer matrix of claim 17, wherein the reinforced structure comprises 3% by weight of soot.
27. The reinforced polymer matrix of claim 26, wherein the soot increases the plasticity at least 6% greater than the hardened polymer structure that has not been reinforced with soot.
28. The reinforced polymer matrix of claim 26, wherein the soot increases the average elastic modulus by at least 8 % over the hardened polymer structure that has not been reinforced with soot.
29. The reinforced polymer matrix of claim 26, wherein the soot increases the hardness by at least 10% over the hardened polymer structure that has not been reinforced with soot.

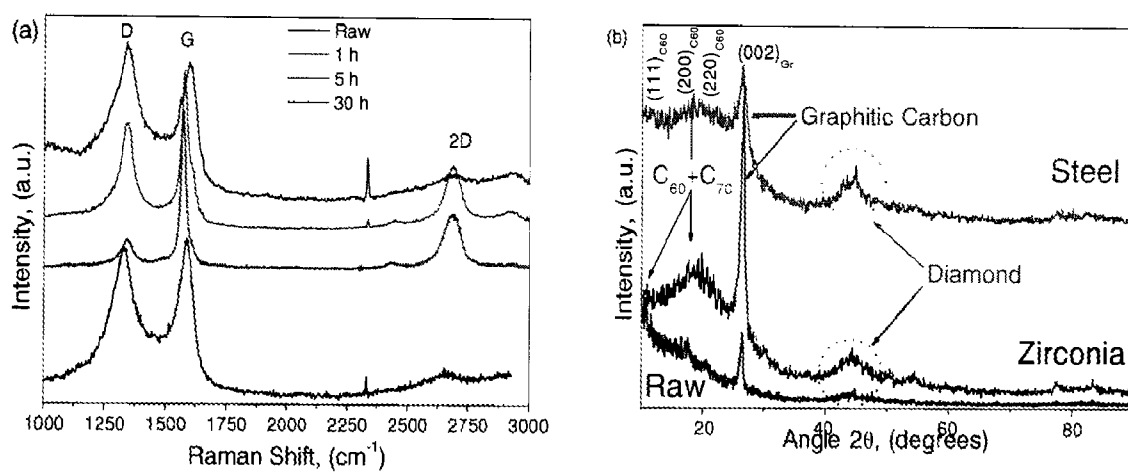


Fig. 1

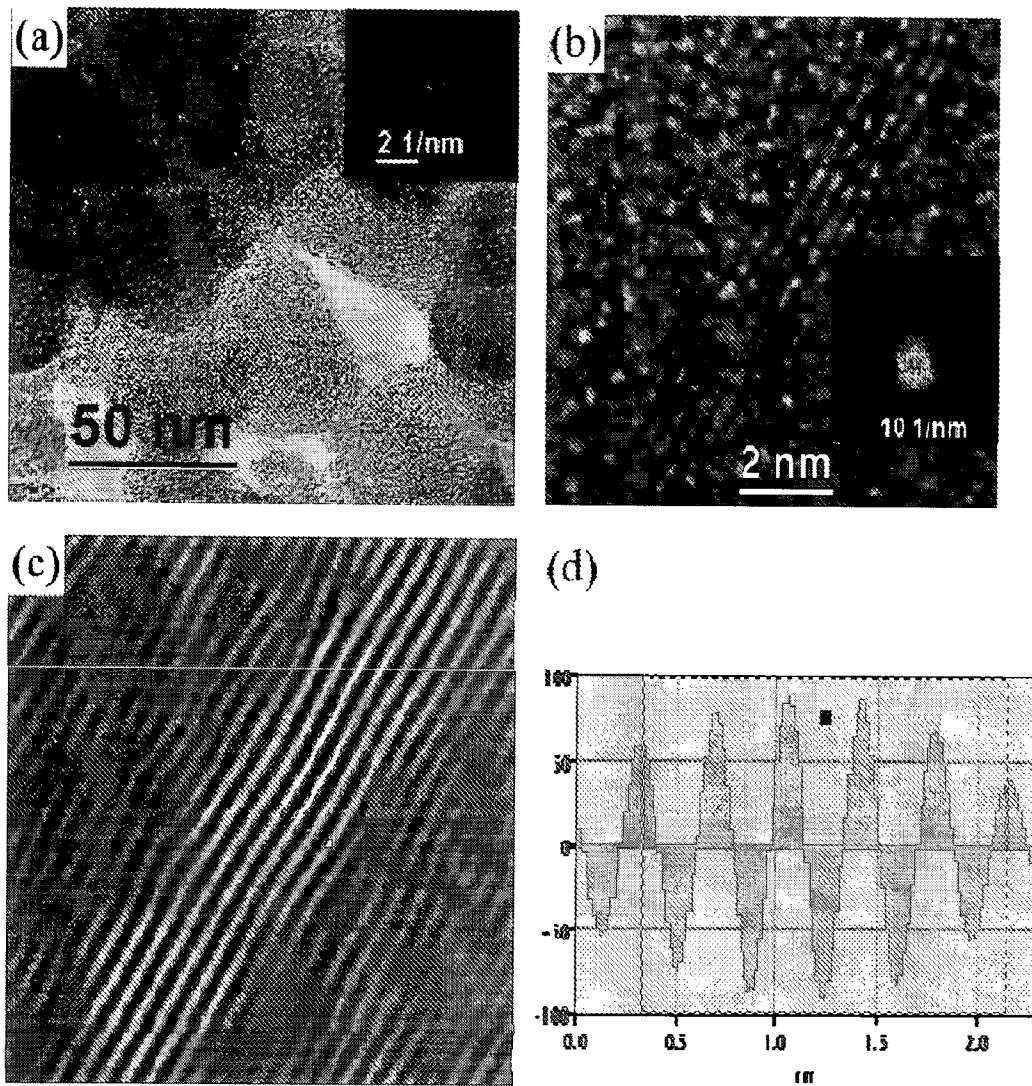


Fig. 2

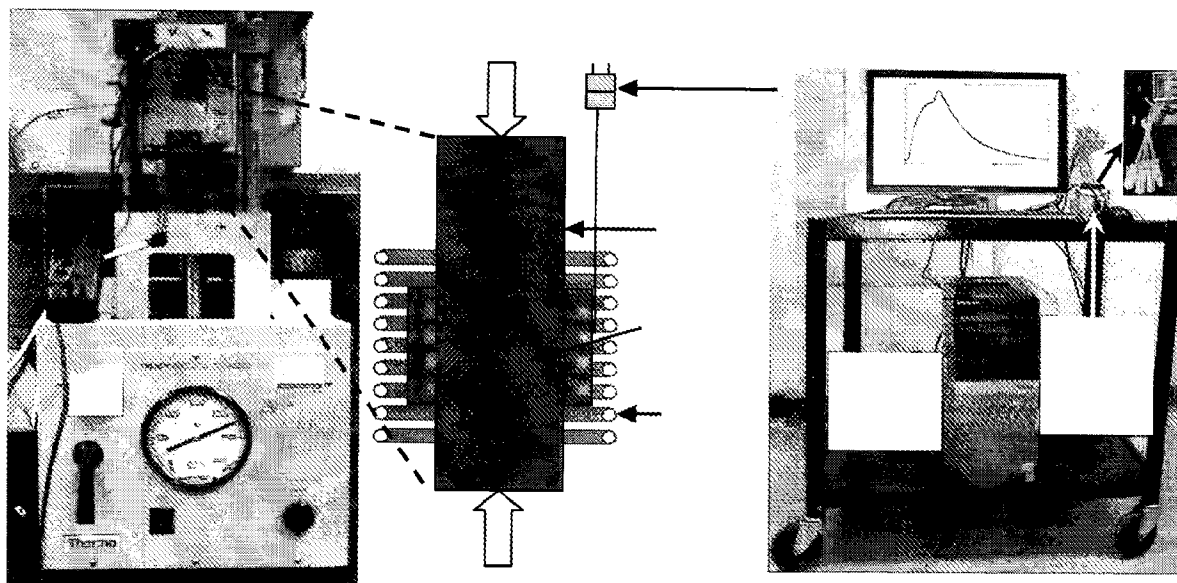
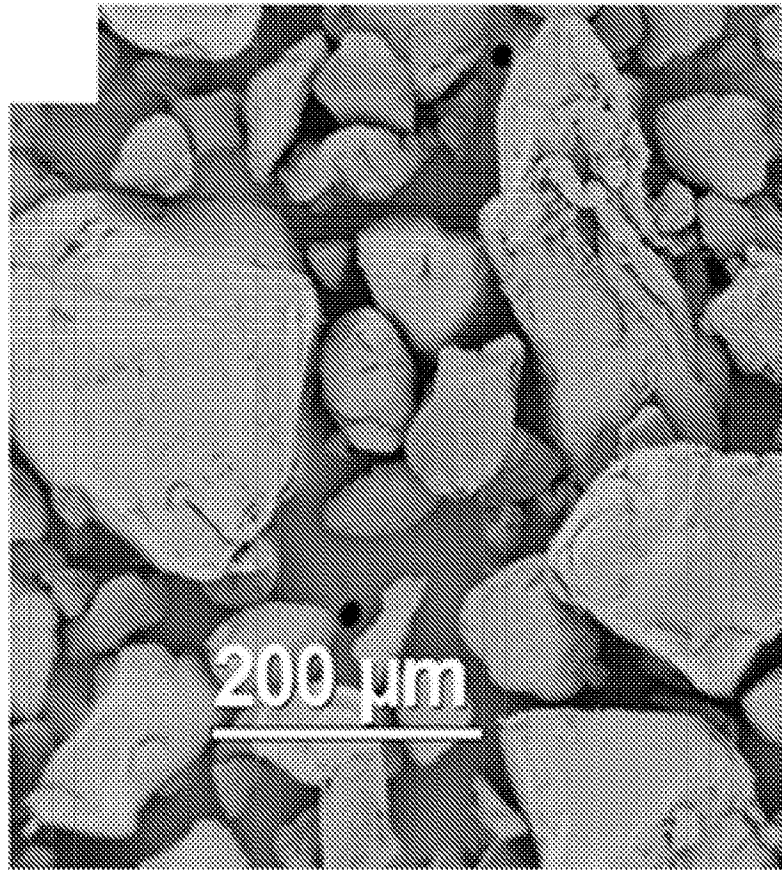


Fig. 3

(a)



(b)

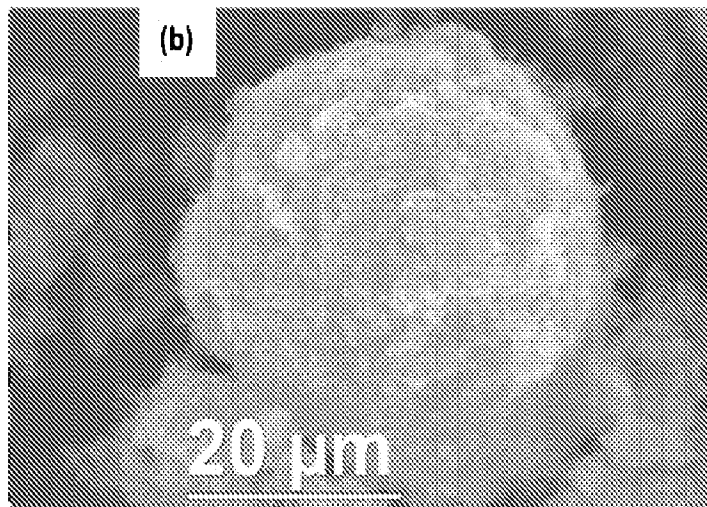


Fig. 4

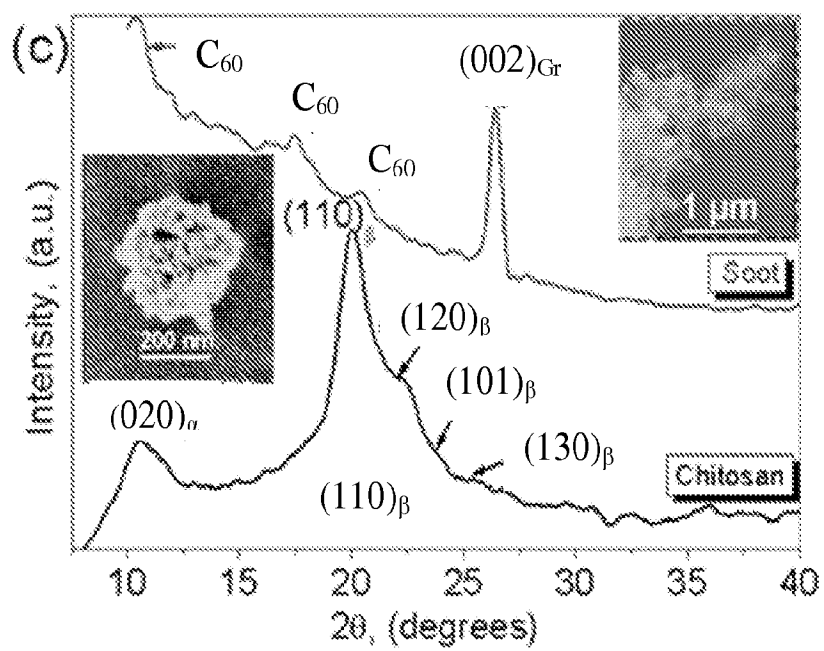


Fig. 4

(d)

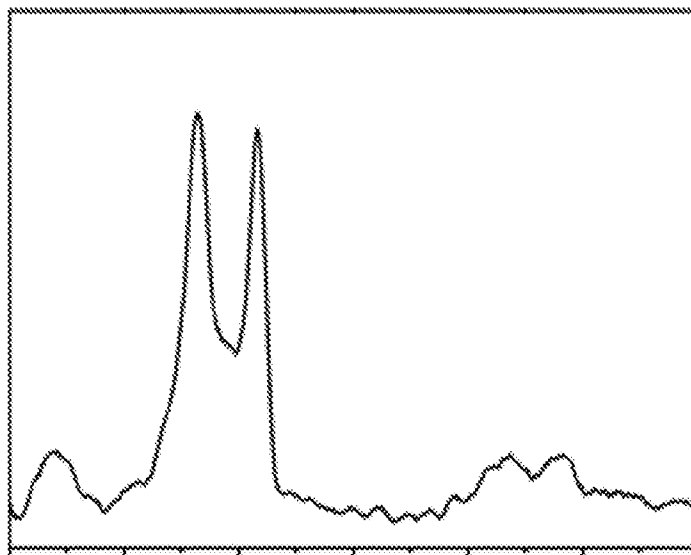


Fig. 4

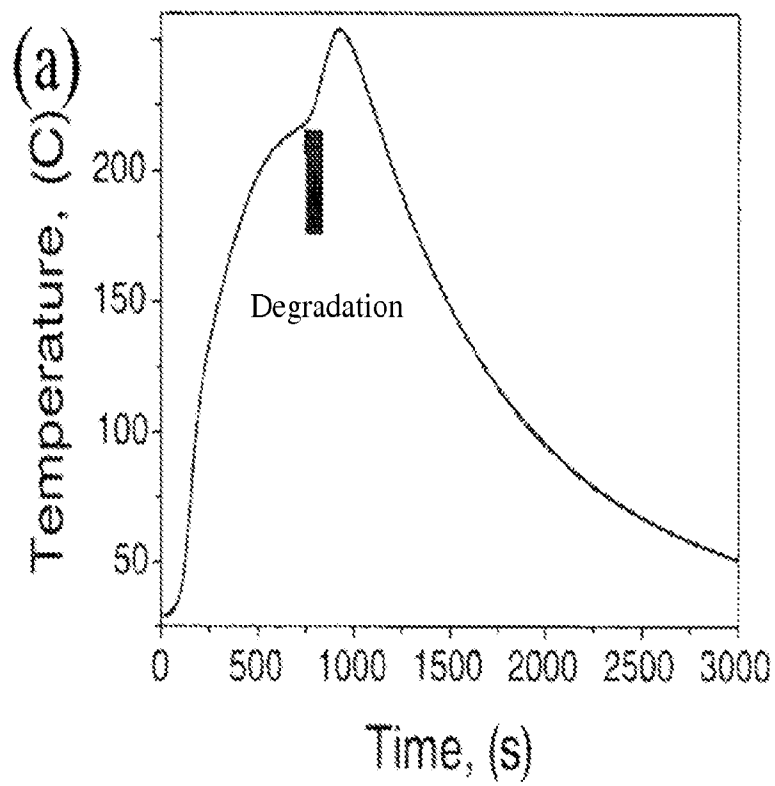


Fig. 5

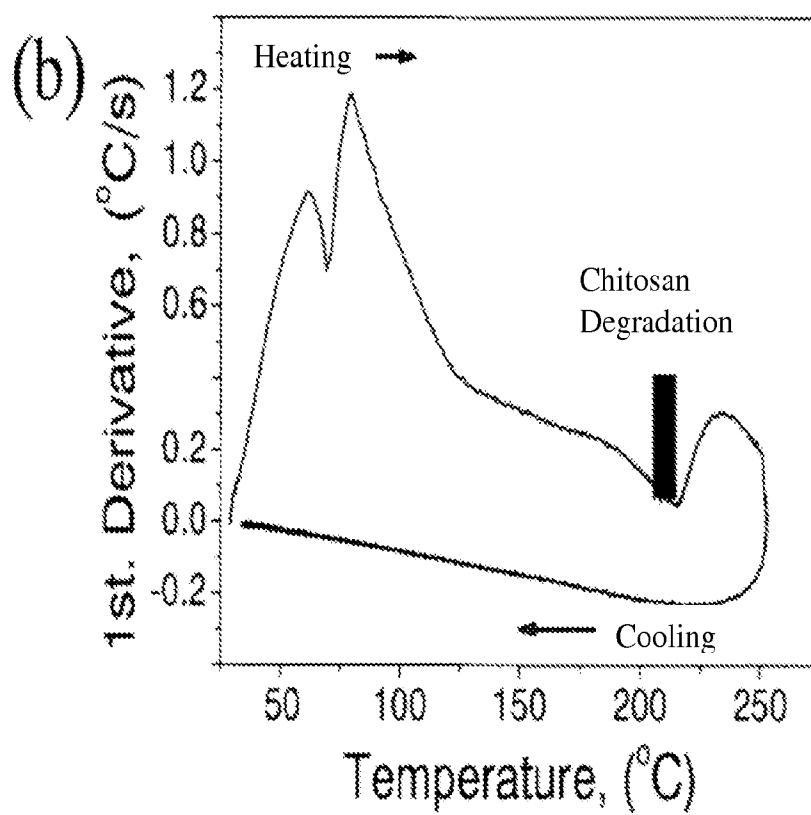


Fig. 5

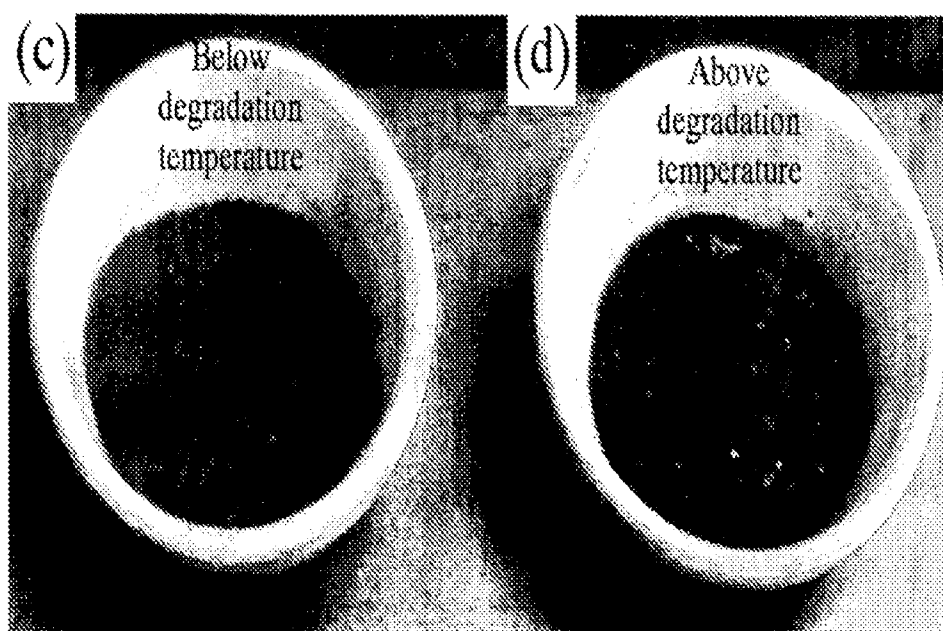


Fig. 5

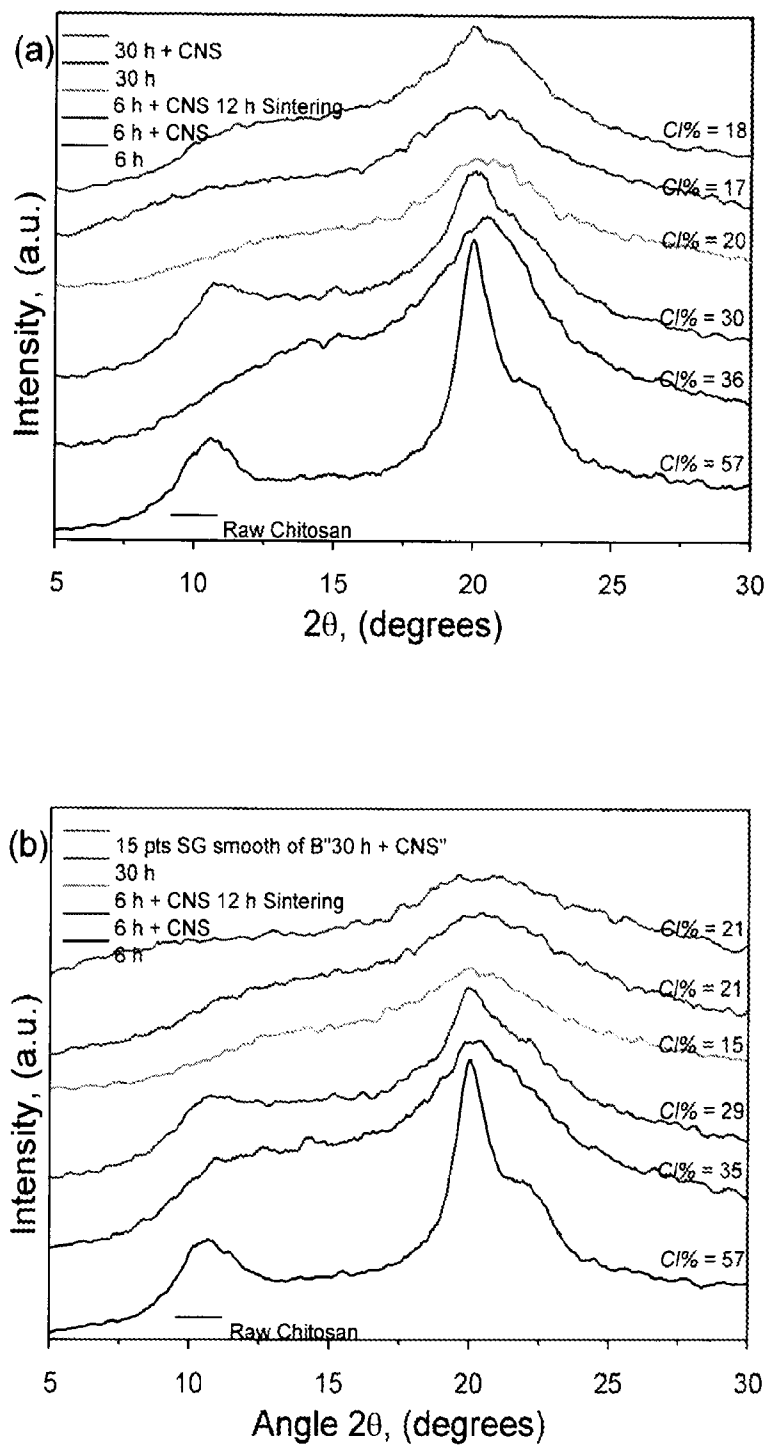


Fig. 6

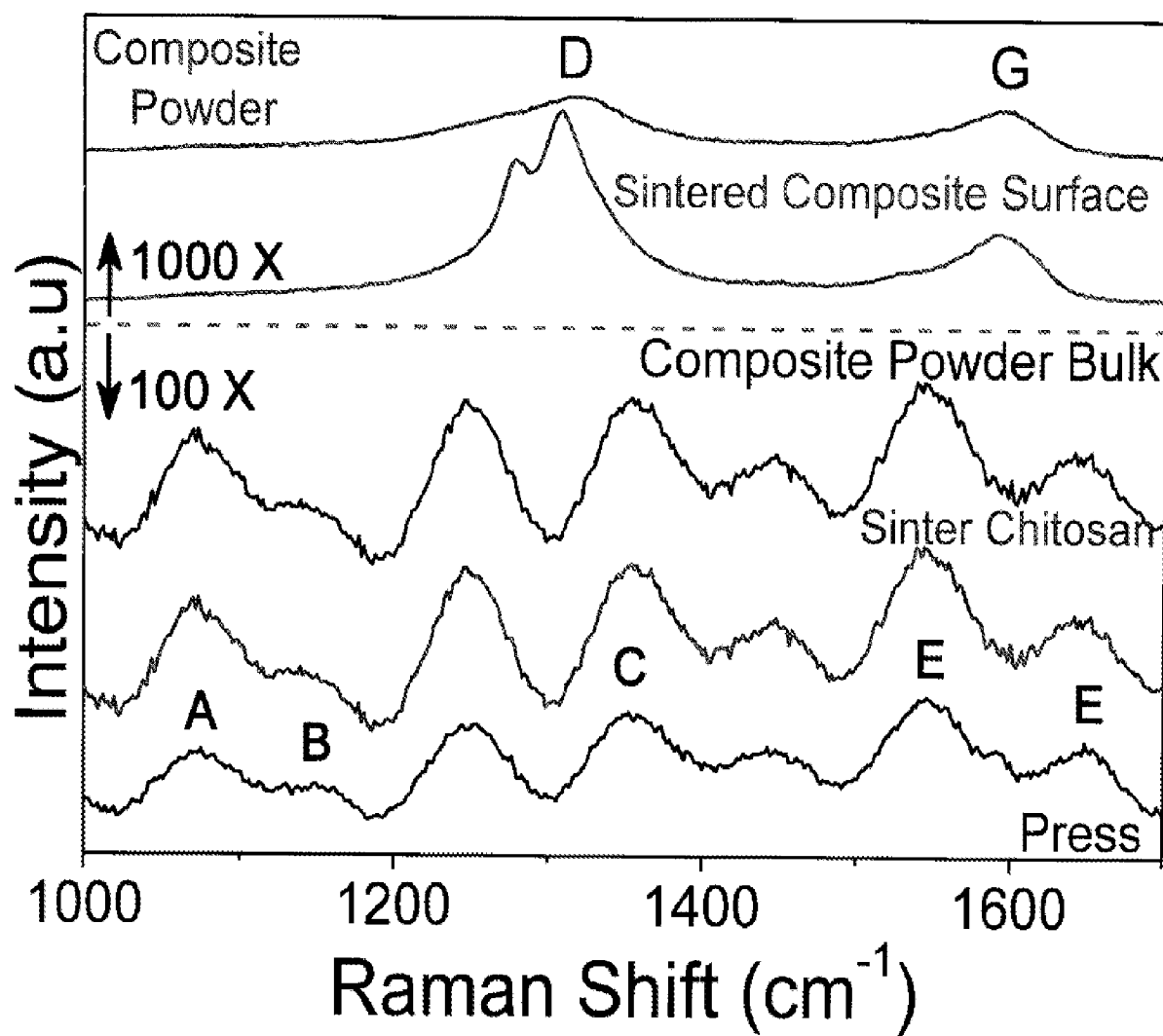


Fig. 7

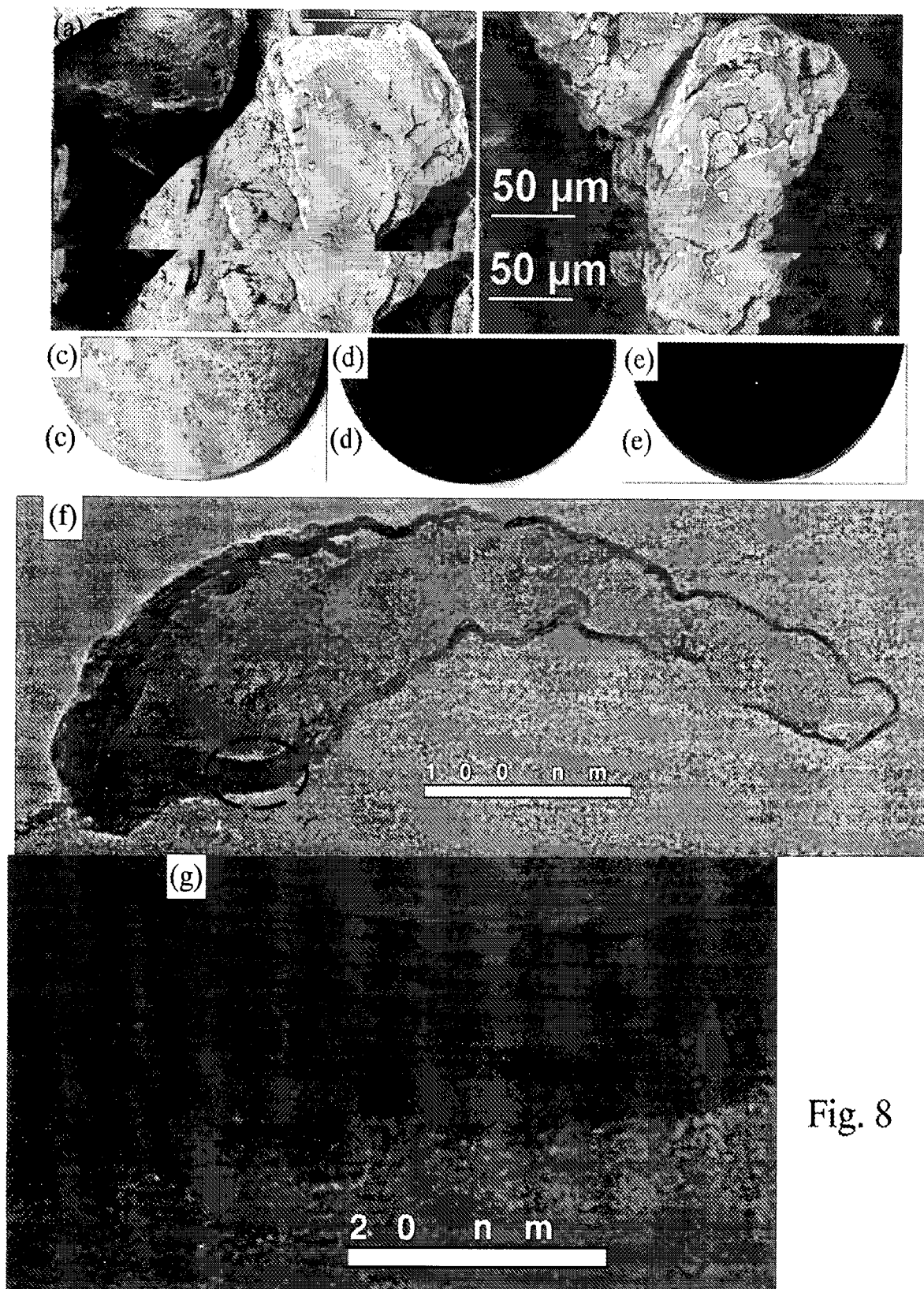


Fig. 8

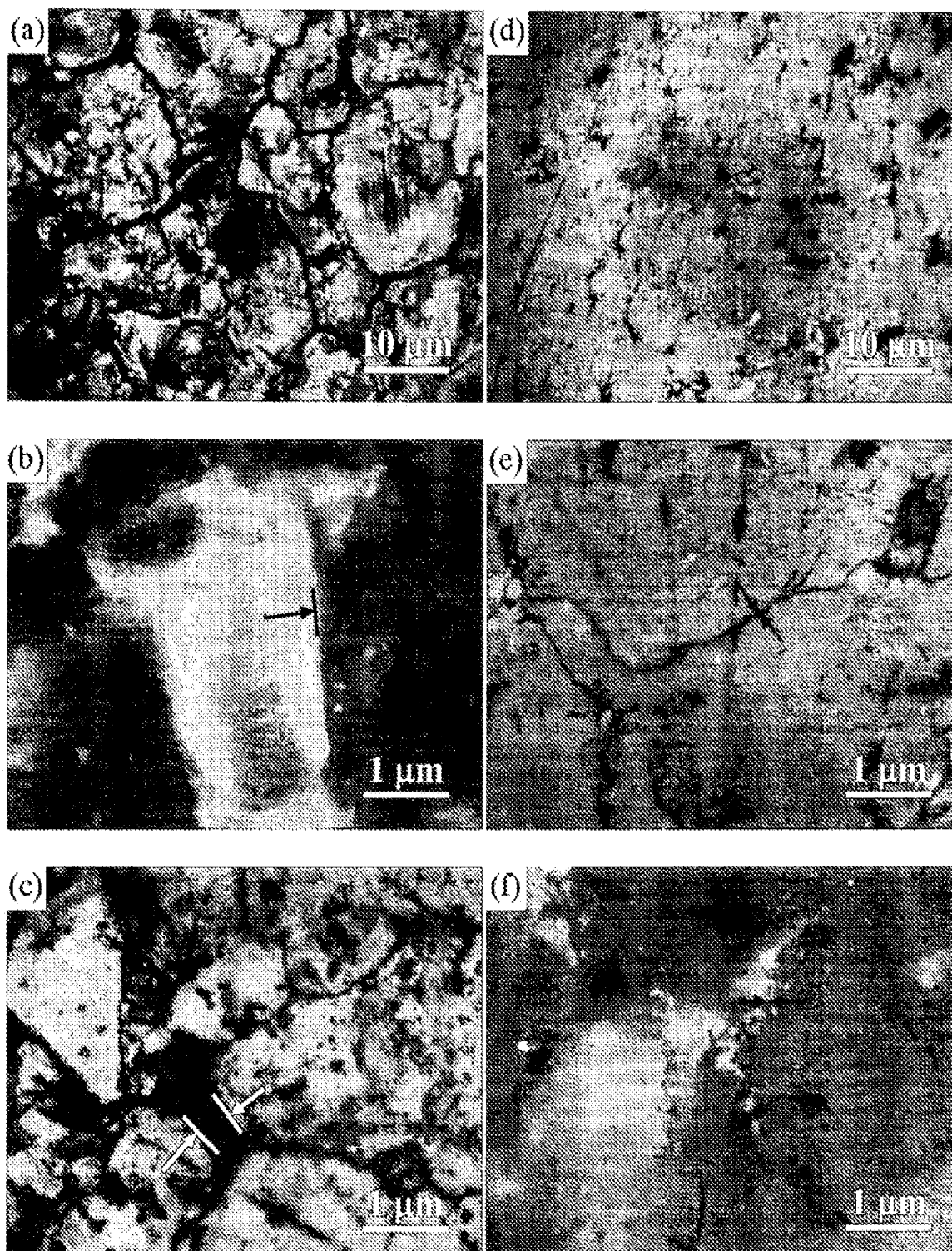


Fig. 9

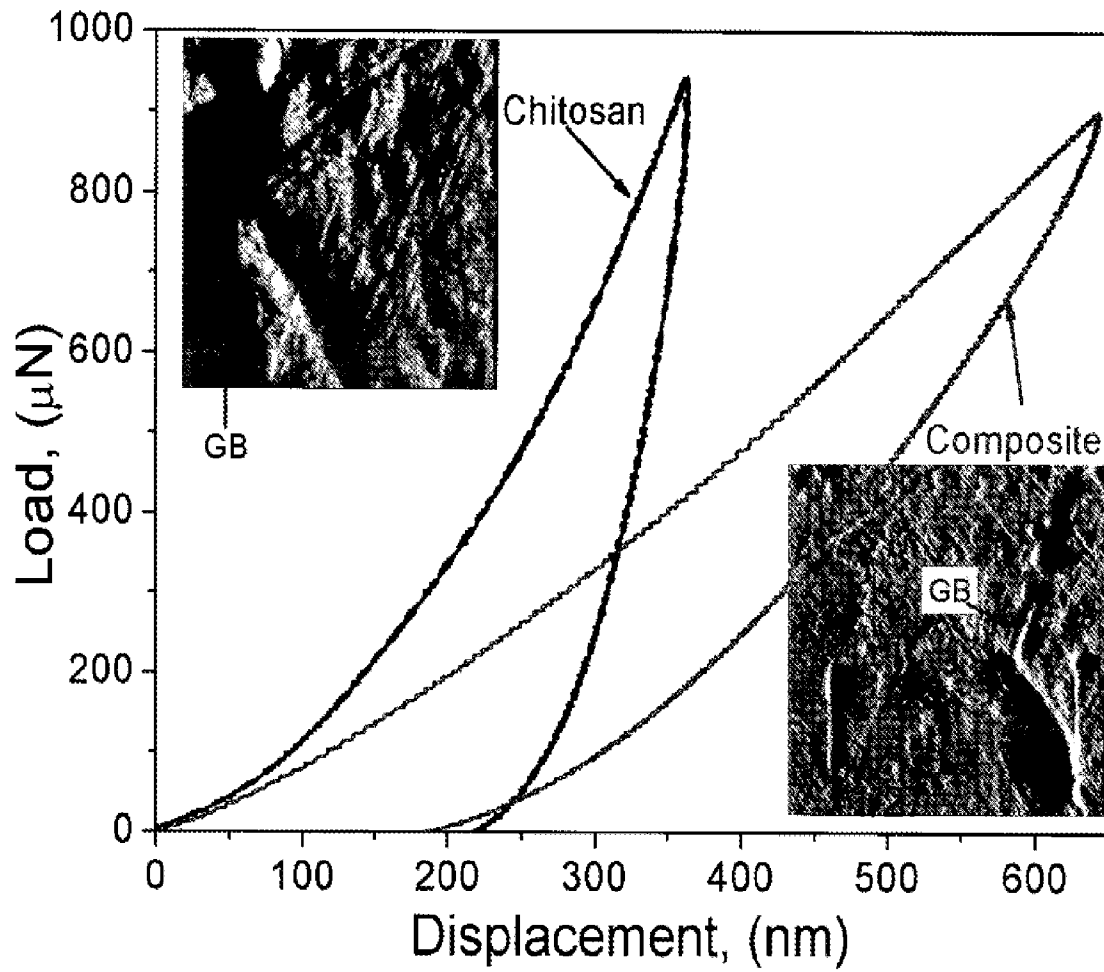


Fig. 10

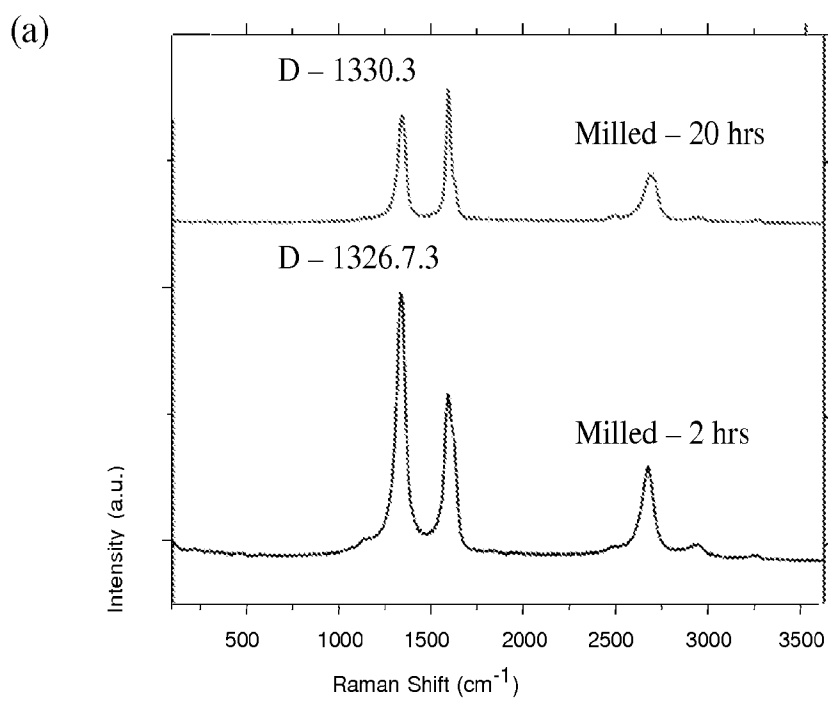


Fig. 11

(b)

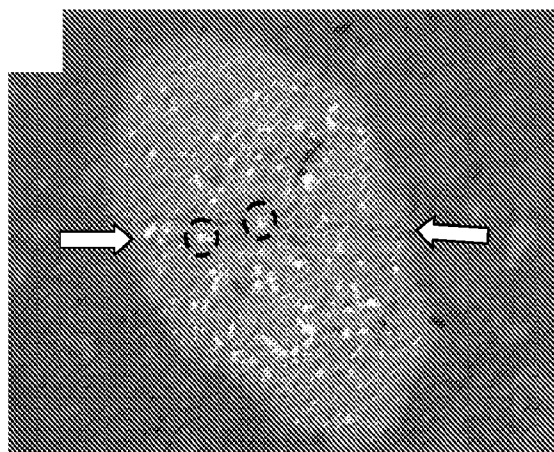


Fig. 11

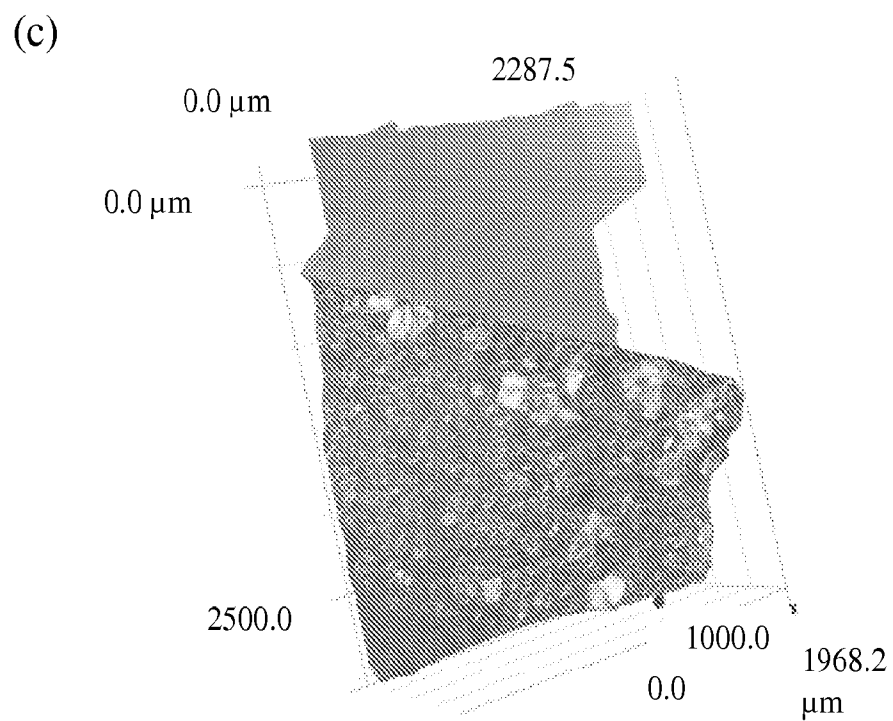
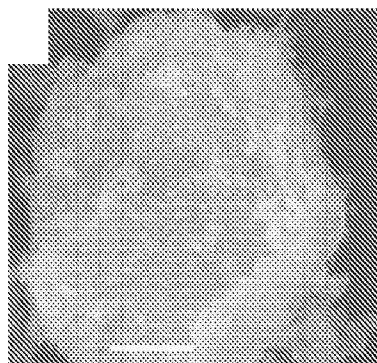
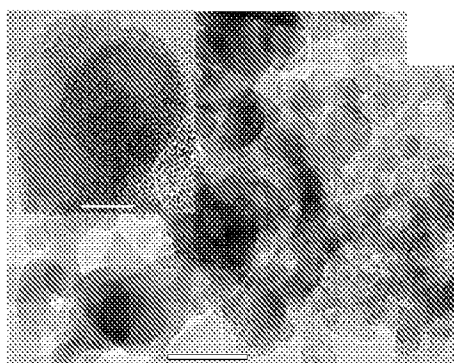


Fig. 11



(a)

10 μ m

(b)

10 μ m

100 nm

Fig. 12

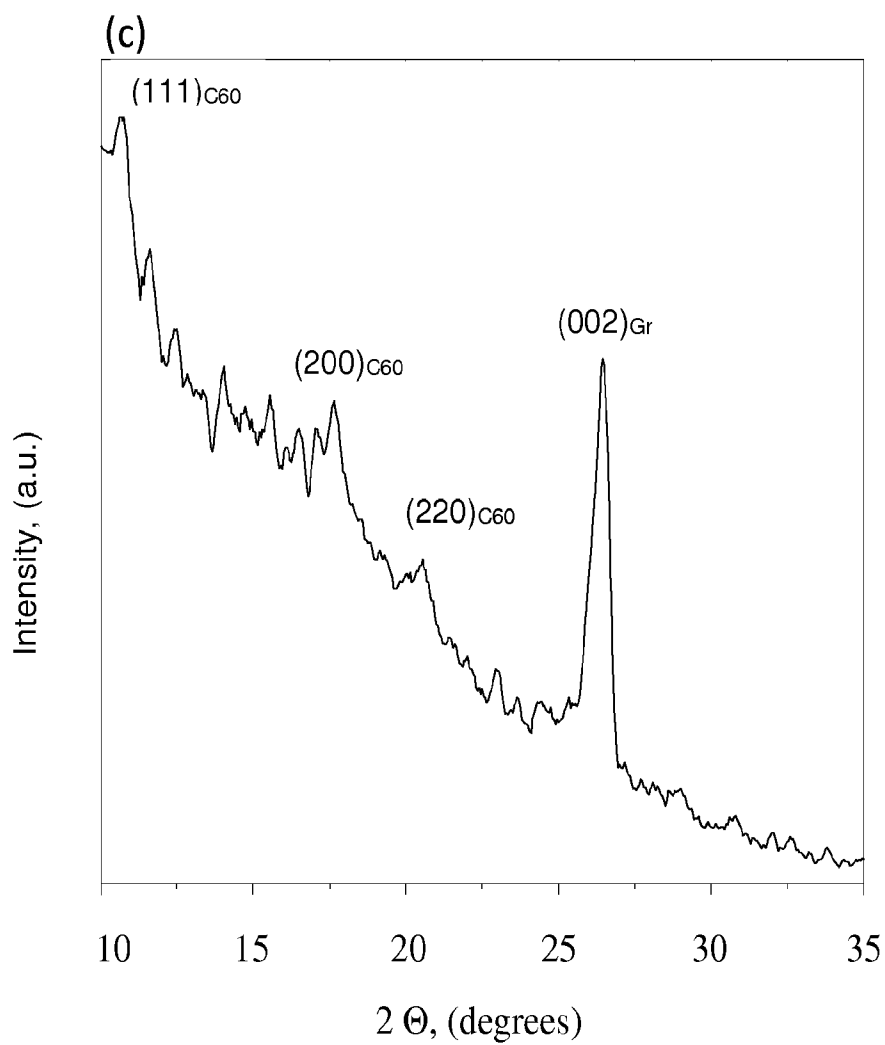


Fig. 12

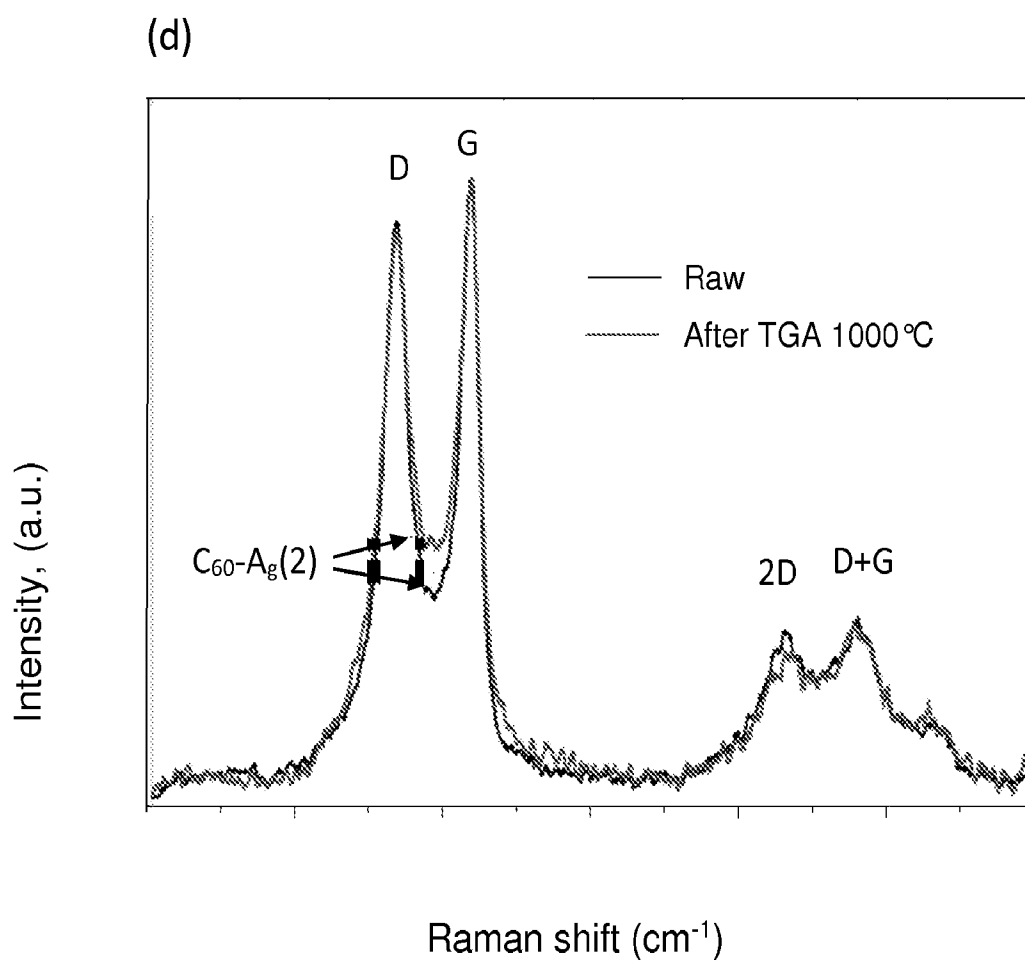


Fig. 12

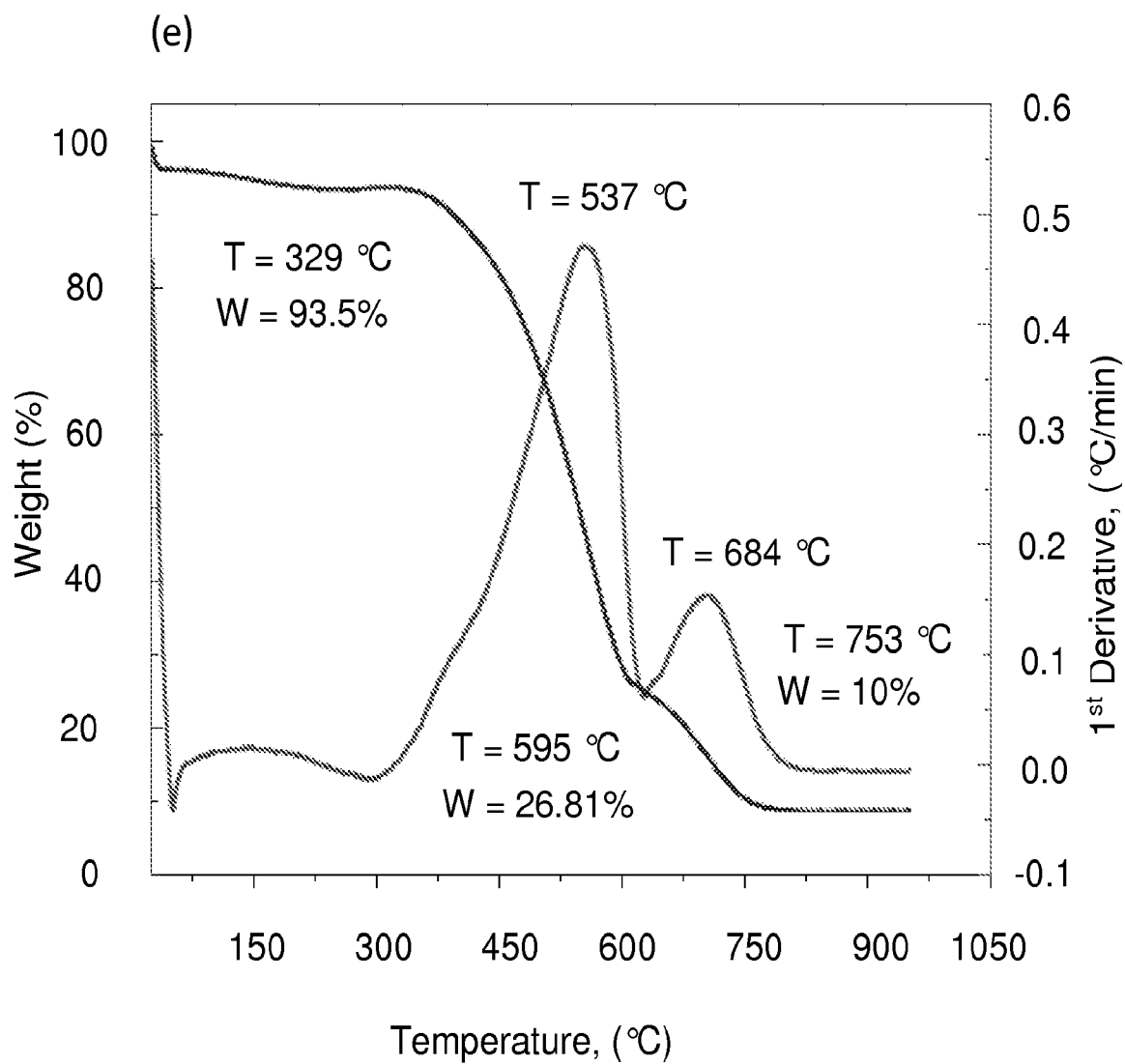


Fig. 12

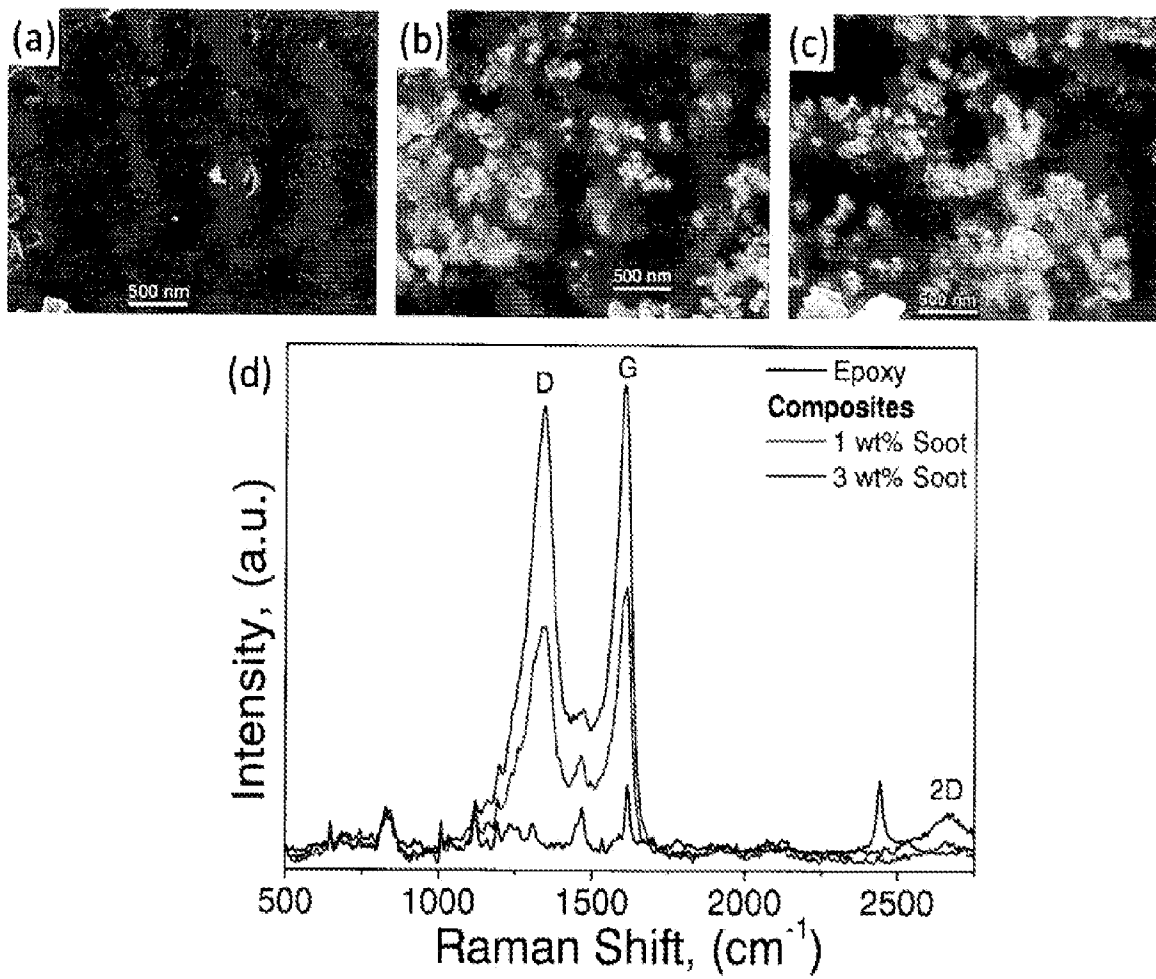


Fig. 13

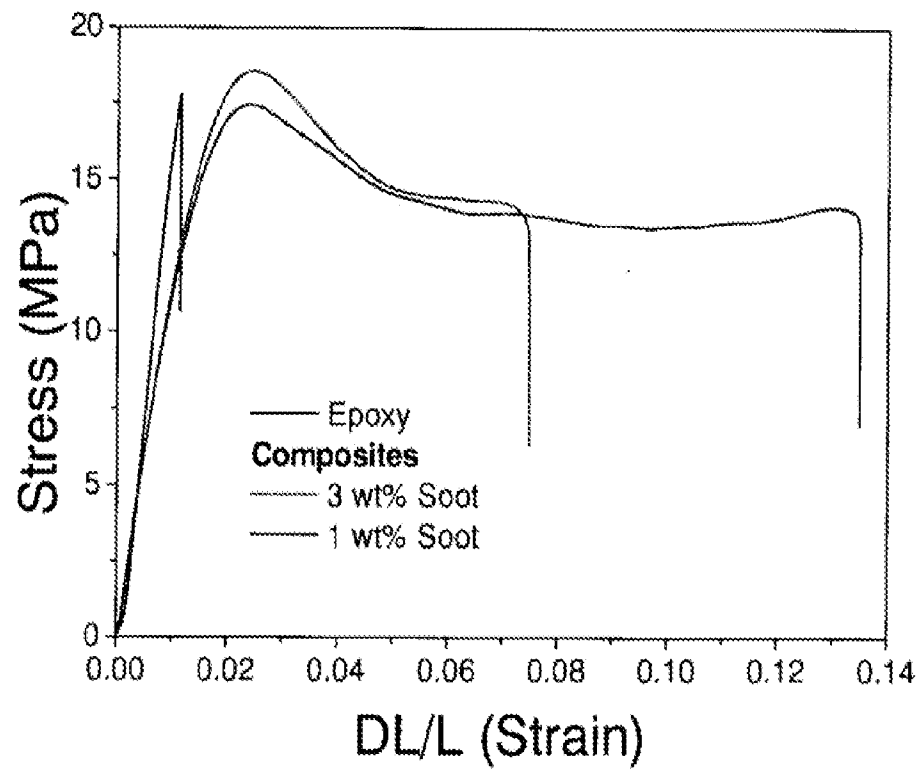


Fig. 14

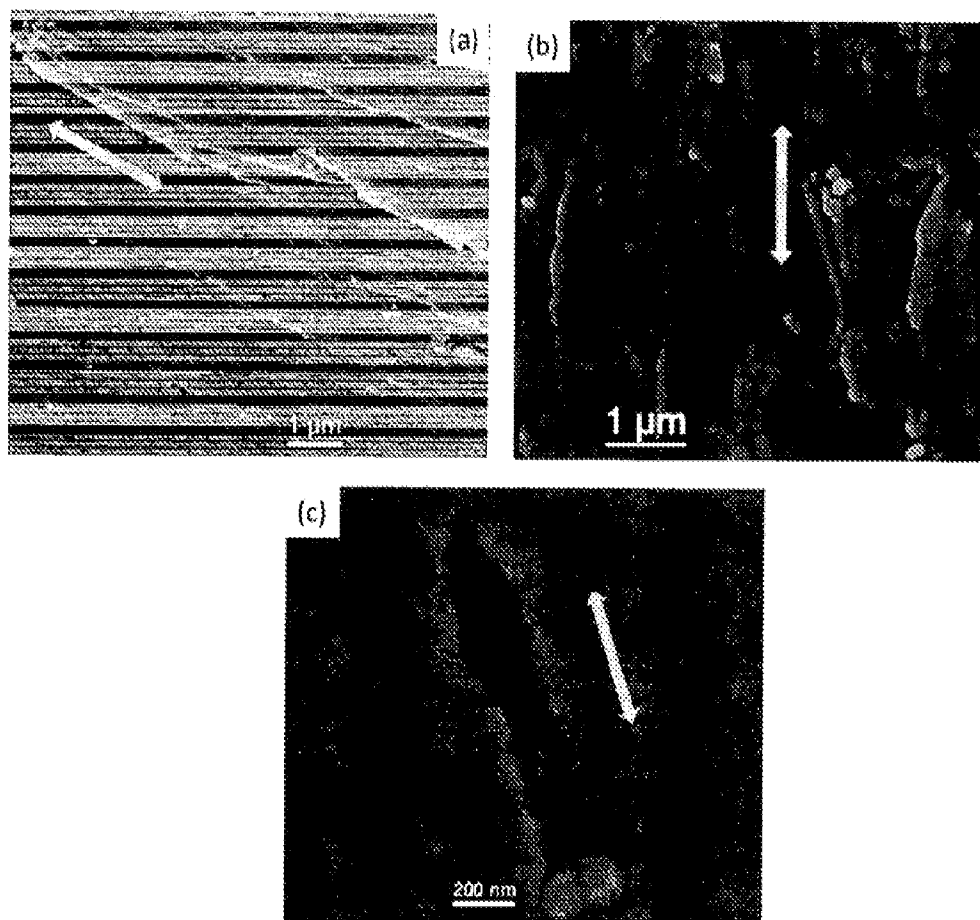


Fig. 15

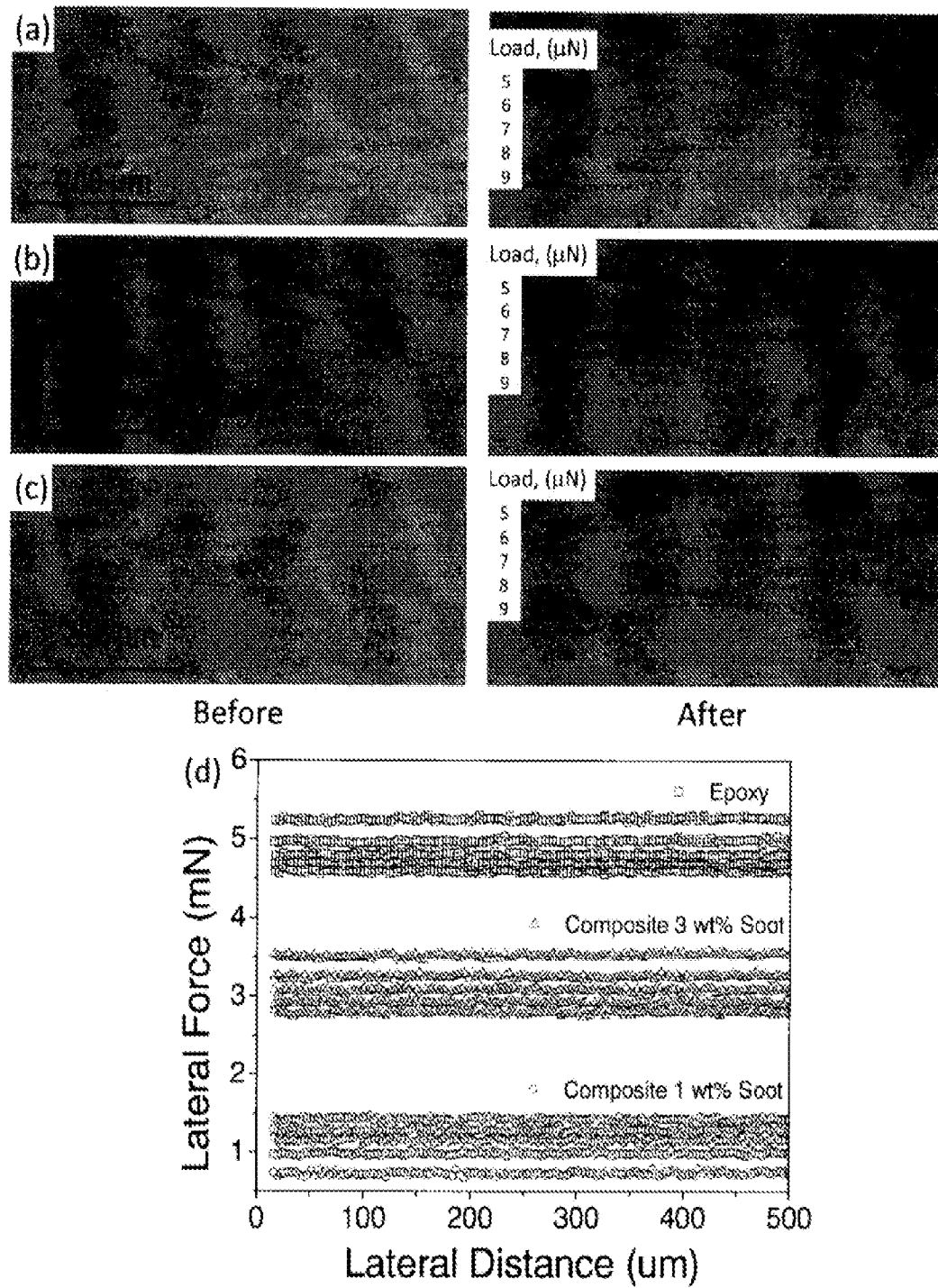


Fig. 16

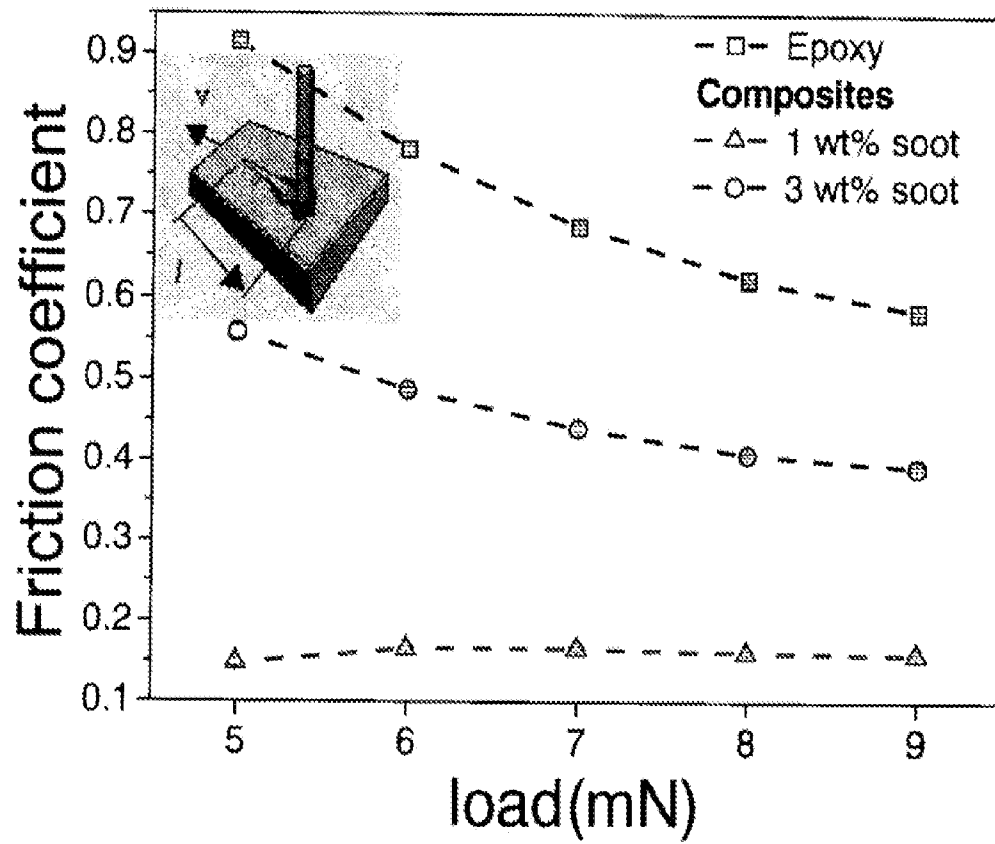


Fig. 17

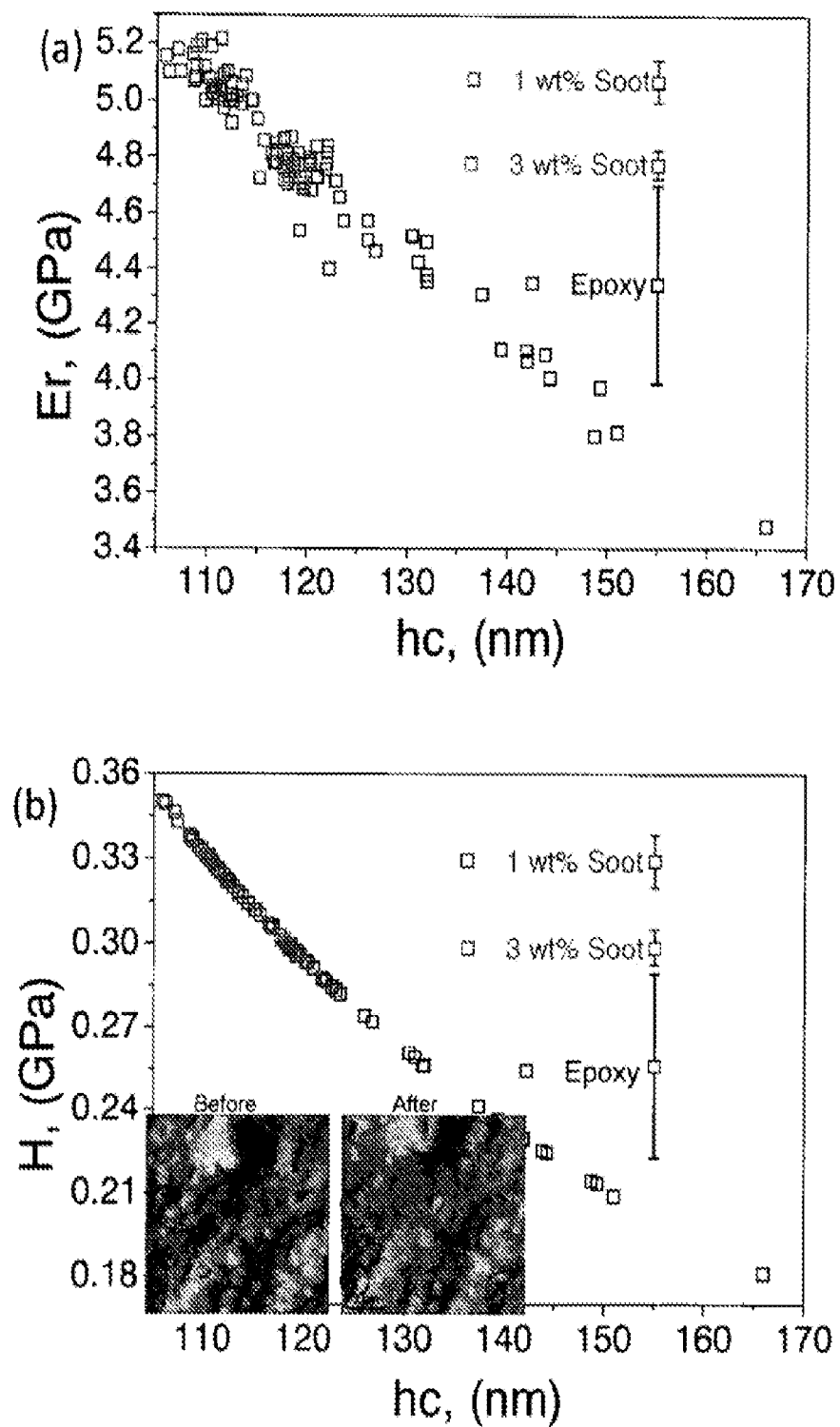


Fig. 18

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2015/022696

A. CLASSIFICATION OF SUBJECT MATTER		
<i>C01B 31/02 (2006.01)</i> <i>C08K 3/04 (2006.01)</i> <i>C04B 35/52 (2006.01)</i> <i>B82Y 30/00 (2011.01)</i> <i>B82Y 40/00 (2011.01)</i>		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
B29C 70/00, 70/04, 70/26, 70/28, B82Y 30/00, 40/00, C01B 31/00, 31/02, 31/04, 35/52, C08K 3/04, 3/08, 3/40, 9/00, 9/02, 13/02, C08J 5/00, 5/12, C09C 1/48, 3/04, 3/06		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
PatSearch (RUPTO internal), USPTO, PAJ, Esp@cenet, DWPI, EAPATIS, PATENTSCOPE, Information Retrieval System of FIPS		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KWANGMIN Choi et al. Mechanical Properties of Aluminum-based nanocomposite Reinforced with Fullerenes. 9th International Conference on Fracture & Strength of Solids, June 9-13, 2013, Jeju, Korea	1-4, 6-16
Y	Slutsker E. M. Adsorbtsionnye svoistva nanostrukturirovannykh uglerodnykh materialov fulleroidnogo tipa. Avtoreferat dissertatsii na soiskanie uchenoy stepeni kandidata nauk. Sankt-Peterburg, 2005, p. 8-9, table 1-2	1-4, 6-16
X	EA 200800197 A1 (CINVENTION AG) 30.06.2008, p. 5, 11-13	17
Y		1, 13, 16, 18-29
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents:	“T”	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“A” document defining the general state of the art which is not considered to be of particular relevance	“X”	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“E” earlier document but published on or after the international filing date	“Y”	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	“&”	document member of the same patent family
“O” document referring to an oral disclosure, use, exhibition or other means		
“P” document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search	Date of mailing of the international search report	
19 June 2015 (19.06.2015)	06 August 2015 (06.08.2015)	
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37	Authorized officer O. Shobanova Telephone No. 499-240-25-91	

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2015/022696

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	RU 2434033 C2 (ZAKRYTOE AKTSIONERNOE OBSHCHESTVO "INNOVATSI Leningradskikh Institutov i Predpriyatiy" (ZAO ILIP) et al.) 20.11.2011, p. 1, 4-7	15, 20-24, 26-28
Y	BUSHUEV Yu. G. et al. Uglerod-uglerodnye kompozitsionnye materialy. Moskva, "Metallurgiya", 1994, p. 15	18-19
Y	IVANOVSKY V. I. Tekhnichesky uglerod. Protsessy i apparaty. Omsk, 2004, p. 6	18-19
Y	POTALITSYN M. G. et al. Modifitsirovanie kaprolona fulleroidnymi materialami. Voprosy materialovedeniya, 2006, №2(46), p. 153-157, abstract	25, 29
A	ATIF TAKHA Mukhammad Farag. Vliyanie gamma-oblucheniya na strukturu, teplofizicheskie i mekhanicheskie svoistva nanouglerodsoderzhaschikh polimerov. Avtoreferat dissertatsii na soiskanie uchenoy stepeni kandidata fiziko-matematicheskikh nauk. Dushanbe, 2012, p. 10-12	1-29