

Research Article

Chemical Functionalization of Helical Carbon Nanotubes: Influence of Sonication Time and Concentrations of Sulfuric and Nitric Acids with 3:1 Mixing Ratio

Sean R. Taklimi , Ali Ghazinezami , and Davood Askari 

Department of Mechanical Engineering, Wichita State University, 1845 Fairmount, Wichita, KS 67260-0133, USA

Correspondence should be addressed to Davood Askari; davood.askari@wichita.edu

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Carbon nanotubes (CNTs) with straight geometries have been widely studied for various engineering applications, and they are often treated or functionalized to improve their effectiveness, depending on their role and expected performance. However, helical configurations of CNTs (HCNTs) have not been sufficiently investigated, especially in their functionalized states for high-performance nanocomposite applications. The coil-shaped geometry of these HCNTs increases the mechanical entanglement of these nanotubes with a host resin system when they are used as reinforcements. This consequently has the potential to improve the mechanical, thermal, electrical, and magnetic properties of the polymeric matrix systems. A uniform dispersion of CNTs in the resin plays an important role in obtaining improved and consistent properties in the final nanocomposite part. To improve the homogeneous dispersion (individual suspension) of these nanotubes in the host resin and to enhance their interactions/bonds with the resin molecules, the surface of these nanotubes should be modified. This study investigates a sonication method for chemical functionalization of HCNTs using a mixture of sulfuric and nitric acids with 3 to 1 mixing ratio [3:1], and it evaluates the effects of acid concentrations and sonication time on the severity of the functionalization process. To evaluate the effectiveness of the process parameters, the functionalized HCNTs (FHCNTs) were examined using several characterization instruments and techniques such as Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR), X-ray Diffraction (XRD), visual dispersion test, and Raman spectroscopy. The characterization results confirmed that the changes in process parameters were mostly effective and the atomic structures of the functionalized HCNTs were successfully altered. All FHCNT samples demonstrated higher dispersion uniformity, increase in Raman I_D/I_G ratios, and changes in the FTIR spectra compared to the pristine HCNTs. Most of the FHCNTs had a reduction in crystallinity, which was consistent with our expectation that functionalization generates more defects on the surface structure of HCNTs, thus leading to a lower intensity of the graphitic peak. The largest reduction in crystallinity was seen for HCNTs treated with a 16 molarity acidic solution; therefore, the HCNTs that were treated with lower molarity acids could be used for further studies and explored for their effective applications in improving the mechanical, thermal, and electrical properties of polymeric nanocomposites.

1. Introduction

Owing to their exceptional properties and characteristics, nanomaterials and nanostructures have played important roles in advancing the science and technologies utilized in many applications including medicine [1, 2], energy storage and conversion [3, 4], nanosensors and devices [5–7], advanced materials [8, 9], and nanocomposites [10, 11]. Among the many types of nanomaterials and nanostructures,

carbon nanotubes (CNTs) have attracted a great deal of interest for applications in high-performance materials and structures, due to their outstanding mechanical [12–14], thermal [15–17], electrical [18, 19], and electromagnetic shielding [20] properties. In general, composite material systems are composed of two main parts: the reinforcement and the matrix. The reinforcement phase primarily handles the external loads, and the matrix phase protects and bonds the reinforcements together and has weak mechanical

properties. Incorporation of CNTs with their unique properties can enhance and tune the properties of polymeric nanocomposites for specific applications. In addition, the low density of 1.3 g/cm^3 [21] of CNTs can be another interesting factor for application of these nanomaterials for improvement of nanocomposite properties, without adding a considerable amount of weight. However, CNTs have nearly perfect crystalline structures that do not have much tendency to form new covalent bonds with polymer molecules. In addition, the presence of Van der Waals attractive forces between the CNTs results in their agglomeration and prevents their uniform dispersion in the resin systems. To solve this problem the sp^2 bond [22] of carbon-carbon on the surface of CNTs should be modified to increase its tendency for bonding to other molecules and materials (e.g., molecular chains of polymeric resins).

To address these issues, covalent functionalization techniques can be used as an effective way of achieving improved bonding and uniform dispersion of CNTs in polymeric resins. This can be accomplished through the alternation of the CNTs' atomic structures and attachment of different functional groups on their side-walls. Carbon nanotubes exist in various geometrical configurations [23–27]; therefore, it is crucial to find appropriate methods and optimum procedures for effective functionalization of CNTs, considering their structural configurations (e.g., straight, helical, and toroidal), characteristics, and the resin systems that they will be incorporated in. There are two main methods for functionalization of CNTs, which are based on physical and chemical functionalization processes [23, 27, 28]. Between these two main categories, chemical functionalization processes are the most commonly used methods, which use different types of strong oxidants to alter the surface of CNTs for attachment of functional groups and improvement of their solubility in liquid resins. Furthermore, one of the advantages of chemical functionalization methods is the increased bond strength between functional groups attached to the surface of CNTs and the resin molecules [27].

A helical carbon nanotube (HCNT) is considered as one of the geometrical configurations of CNTs, which is the focus of this study. According to their structural shape, these HCNTs have the potential to be used for a variety of applications such as medical devices, solenoids, shock absorbing devices, cellular technology, electromagnets [29–31], and nanocomposites [23–27, 32]. Furthermore, their coil shape gives them the ability to respond to the external loads like a coil spring that can sustain large deformations and return to their original shape and length after unloading. Therefore, helical CNTs have a good potential to deliver good mechanical properties and especially higher fracture toughness compared to the straight CNTs, when they are used as additional reinforcements in composite material systems [33]. In addition, a different study showed that HCNTs can be used for improving the microwave absorbing properties of composites [34]. It is worth mentioning that the helical CNTs can interlock within the resin system, once they are used as reinforcements, and they cannot be easily pulled out of the resin, due to their geometrical configuration [25, 26]. Furthermore, they can be entangled and mechanically interlocked with

each other and the microfiber reinforcements in addition to being stuck in the surrounding cured resin. However, they suffer from weak interface bonding with the surrounding resin, due to their inertness and lack of tendency for formation of new chemical bonds. To address this issue, chemical functionalization can be used to chemically functionalize the helical CNTs and improve their interface bonds with the surrounding resin molecules.

The lack of technical information and reports related to chemical functionalization of helical CNTs was one of the main triggering factors for performing this research. It should be mentioned that helical configurations of HCNTs are formed due to the existence of periodically repeated pentagonal/heptagonal carbon rings, which is the indication of atomic defects on their side-walls that are formed during the synthesis process [14]. These defects make the chemical functionalization of HCNTs quite different from the chemical functionalization of straight CNTs, meaning that it requires special consideration regarding the selection of chemical functionalization method and the processing parameters [23–25, 32, 33]. A number of chemical functionalization methods (e.g., sonication and refluxing processes) and processing parameters (e.g., acid types, solution mixture composition, mixing ratios, acid molarities, processing temperature, and processing time) were studied [23–27, 32] to investigate their effectiveness on covalent functionalization of straight CNTs and HCNTs for applications as reinforcements in polymeric nanocomposites. In this study, a chemical functionalization process was used, whereby, HCNTs were sonicated with a mixture of sulfuric and nitric acids (i.e., an acidic mixture with 3 to 1 mixing ratio [3:1]) with different molarities (i.e., 3, 8, and 16 M) and processing times (i.e., 3, 6, and 9 hrs). Note that the acid molarities and time duration of the sonication process were considered as the variable parameters, and their effects on chemical functionalization of HCNTs were studied for nanocomposites applications. For the characterization of chemically functionalized HCNTs, Scanning Electron Microscopy (SEM), a visual dispersion test, Raman spectroscopy, X-ray Diffraction (XRD), and Fourier-Transform Infrared (FTIR) spectroscopy were used to evaluate the extent and quality of the functionalization processes. It was also intended to make sure that the treated HCNTs have maintained their graphitic crystalline structures and that functional groups are attached to their side-walls. Based on the characterization results, the effectiveness of the functionalization technique along with the influence of each process parameter were investigated.

2. Chemical Functionalization of Helical CNTS

2.1. Materials and Instruments. CNTs with helical configuration was purchased from Cheap Tubes Inc. with outside diameters ranging from 100 nm to 200 nm, the helical coil pitches ranging from 500 nm to 1000 nm, the lengths ranging from 1 to 10 μm , and purity of more than 90%. For vacuum filtration of HCNTs solutions, a 0.4 μm polycarbonate filter was obtained and used from Fisher Scientific. For characterization of chemically functionalized HCNTs, various

instruments and tools were utilized. A JEOL JSM-6460 LV scanning electron microscope was used for imaging of the FHCNTs. The XRD and Raman spectra were acquired using a MiniFlex diffractometer from the Rigaku Corporation and an XploRA™ PLUS microscope from the HORIBA company, respectively. Finally, two modules (Smart OMNI-Sampler and DuraSampler from Thermo Scientific Company) were used for obtaining the FTIR spectrum of the FHCNTs.

2.2. Functionalization Process. A sonication process with a mixture of sulfuric and nitric acid solution with 3 to 1 mixing ratio [3:1] was used for functionalization of HCNTs. The HCNTs were weighed and then added to the acid solution in a closed-cap container. Acid molarities (i.e., 3, 8, and 6 M) and sonication time (i.e., 3, 6, and 9 hours) were the two parameters which were investigated during the functionalization processes. The temperature during the sonication process was kept constant at 60°C. After the completion of the sonication process, the functionalized HCNTs were filtered using a vacuum filtration process. To verify that no acid remained in the filtered solution, the pH of the outlet water was checked continuously by a pH meter. In the last stage, the filter and trapped powder of functionalized HCNTs were placed in an oven at 120°C for 4 hours for drying. The dried HCNTs were separated from the filter and then kept in a closed-cap glass container for further characterization. Figure 1 displays the schematic of the chemical functionalization method along with the processing parameters used in this study.

3. Characterization Results and Discussions

3.1. Visual Dispersion Test. The main objectives of the chemical functionalization of nanomaterials are to improve their dispersion uniformity and suspension stability in different solutions and liquid resins. These are important requirements for successful incorporation of nanomaterials in polymeric composites, as reinforcements. The visual dispersion test is an easy and repeatable technique for assessment of the solubility and suspension stability of nanomaterials in solutions. Small amounts of chemically functionalized HCNTs were added to DI water inside closed-cap glass containers and then sonicated for certain periods of time. Later, these glass containers with FHCNTs solutions were placed on a stable platform and kept still to record their sedimentation rate after specific time intervals. Figure 2 compares the dispersion uniformity and suspension stability of the functionalized HCNTs using different processes after one-week suspension in DI water. As it can be seen, the dispersion of functionalized HCNTs was fairly uniform for all functionalized HCNTs compared to the pristine HCNTs. In addition, the suspension of these FHCNTs did not change after one week. This confirms that our chemical functionalization processes (i.e., sonication with [3:1] mixture of sulfuric and nitric acids with different molarities) were successful for uniform dispersion and prolonged suspension of HCNTs in a liquid.

3.2. Raman Spectroscopy. Raman spectroscopy is a technique used for identifying any disorder or change in the sp^2 carbon-carbon bonds [35]. Carbon nanotubes usually reveal two main peaks: D-band (1330 cm^{-1}) and G-band (1580 cm^{-1}), which are associated with the defect and graphitic structure, respectively, and the ratio of these two peaks can be used to evaluate the effectiveness of the employed chemical functionalization processes [36–39]. Here in this study, strong acids (i.e., sulfuric and nitric acids) were used to generate vacancy defects on perfect/inert crystalline structures of the HCNTs, which later can be used for attaching different functional groups. The existence of appropriate functional groups on the surface of functionalized HCNTs can lead to their improved solubility and dispersion uniformity in different resin systems. Figure 3 presents and compares the two Raman spectral peaks of the functionalized HCNTs samples with respect to the pristine HCNTs; in addition, it illustrates the ratio of (I_D/I_G) bands. Based on these results, the ratio of (I_D/I_G) bands was increased for all functionalized HCNTs. This can be considered as an indication that the functionalization processes employed in this study were successful in generating more side-wall defects on the surface of HCNT structures.

In addition, it can be observed that for most of the FHCNTs samples the increase in molarity led to the reduction of I_D/I_G ratios. This can be seen for all samples which were sonicated for 9 hrs. The FHCNTs samples that were sonicated for 6 hours showed a higher I_D/I_G value when 8 M acidic solution was used. In most cases, the ratio of I_D/I_G was reduced by increasing the sonication time. However, the FHCNTs samples that were sonicated with 3 M and 8 M acids showed lower I_D/I_G values than what was anticipated. It should be noted that the entanglement mechanisms of HCNTs can affect the I_D/I_G values obtained from Raman spectroscopy [27]. Due to their helical geometries with various coil diameters, some of the smaller HCNTs might get fully encapsulated inside larger diameter HCNTs and be protected. This can create some inconsistencies for the Raman spectroscopy results. However, all functionalized HCNTs showed an increase in their I_D/I_G values, which can be considered as a proof of their successful functionalization.

3.3. Fourier-Transform Infrared (FTIR) Spectroscopy. During the chemical functionalization process, the HCNTs go through surface modifications (i.e., the creation of atomic defect). Various functional groups can attach to the side-wall structures of the treated HCNTs, which can consequently lead to improved dispersion of these HCNTs in polymeric resins and give better/stronger interactions (i.e., interface properties/bonds) with polymer molecules. The FTIR is a qualitative technique that was used to distinguish attachments of various functional groups on the surface of HCNTs. In general, the functionalization process leads to changes in four regions of the FTIR spectra. These four regions are (-C-O) stretch between 1000 and 1300 cm^{-1} [36, 40, 41], (-C=C) aromatic stretch between 1500 and 1600 cm^{-1} [40–42], (-C=O) carboxylic acids between 1650 and 1730 cm^{-1} [36, 40, 41, 43, 44], and (-O-H) carboxylic acids hydrogen stretch between 2400 and 3400 cm^{-1} [37,

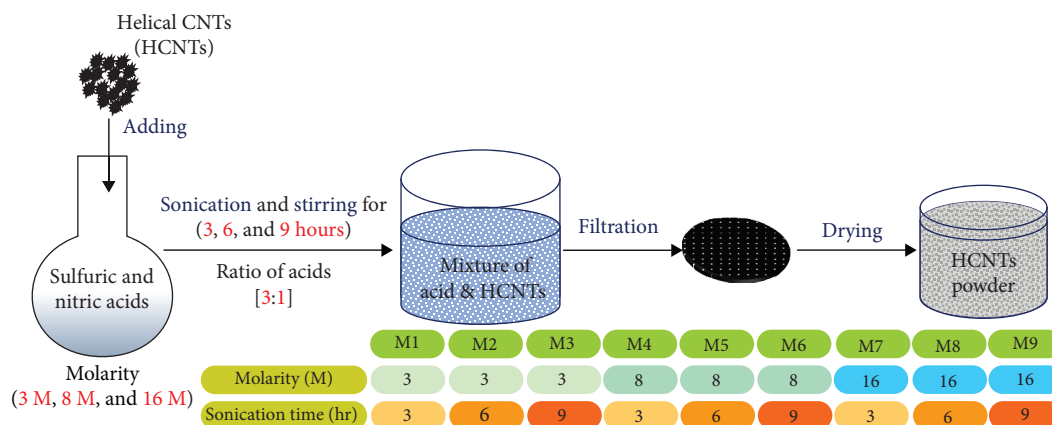


FIGURE 1: Schematic of the chemical method and the processing parameters used for covalent functionalization of HCNTs.

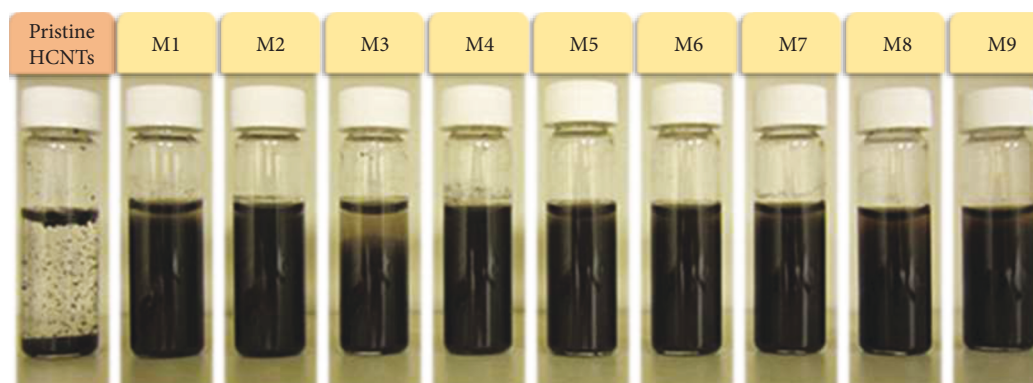


FIGURE 2: Comparison of the dispersion uniformity and suspension stability of the pristine and chemically functionalized HCNTs in DI water after one-week seating time.

41, 42, 45]. Figure 4 shows the FTIR spectra of the chemically functionalized HCNTs in comparison to the pristine HCNTs sample.

For the HCNTs that were functionalized using M7, M8, and M9 procedures (i.e., treated with a 16 M acidic solution), a clear change was observed in all regions of the FTIR spectra, except in the (-O-H) carboxylic acids hydrogen stretch between 2400 and 3400 cm^{-1} spectrum. All other functionalization procedures (i.e., M1 through M6) showed small changes in their spectra compared to the pristine HCNTs sample. Overall, the presented results in this section confirmed that the employed functionalization processes used in this research (i.e., sonication with a [3:1] mixture of sulfuric and nitric acid solutions with 3, 8, and 16 molarities for 3, 6, and 9 hours processing times) were successful in surface modification of the HCNTs, where side-wall defects were generated and various functional groups were attached. This will lead to improved interaction of HCNTs with polymeric resin molecules and enhance their dispersion uniformity for nanocomposites applications. However, using a stronger acidic solution with 16 molarity created a more substantial change in the FTIR spectra that could be an indication of severe side-wall defects on the surface of HCNTs structures.

3.4. X-Ray Diffraction (XRD). The main objective for incorporation of chemically functionalized HCNTs into the resin systems is to enhance their mechanical properties and consequently, to improve the performance of polymeric nanocomposites for structural applications. The use of strong oxidants for chemical functionalization can lead to a reduction in crystallinity of the treated HCNTs (i.e., because of the generation of side-wall defects on the surfaces of CNTs) and hence, degradation of their mechanical properties and integrity. Therefore, it is essential to evaluate the structural crystallinity of functionalized HCNTs and make sure that they are not destroyed because of the exposure to strong acids. Here, XRD can provide valuable information about the purity of materials, dimensions of the unit cells, the structural crystallinity of materials, and physicochemical aspects of any configurations of CNTs [46–48]. In the case of CNTs, the data always demonstrates a big and sharp peak around 26°, which is related to the hexagonal graphitic structure [49, 50]. The intensity of these peaks and their comparison to pristine HCNTs can be used as a valuable indicator for crystallinity of the functionalized HCNTs samples. It should also be mentioned that the presence of any amorphous carbon or defects can change the intensity of this peak [51].

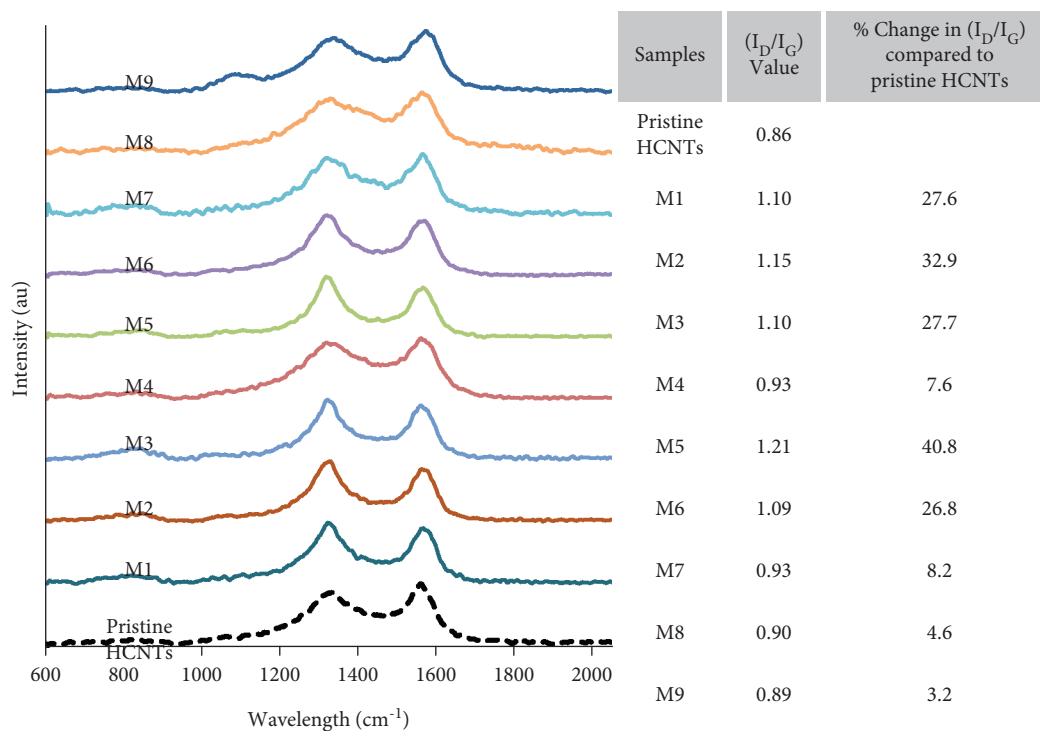


FIGURE 3: Results of Raman spectra and (I_D/I_G) ratio values of pristine and chemically functionalized HCNTs.

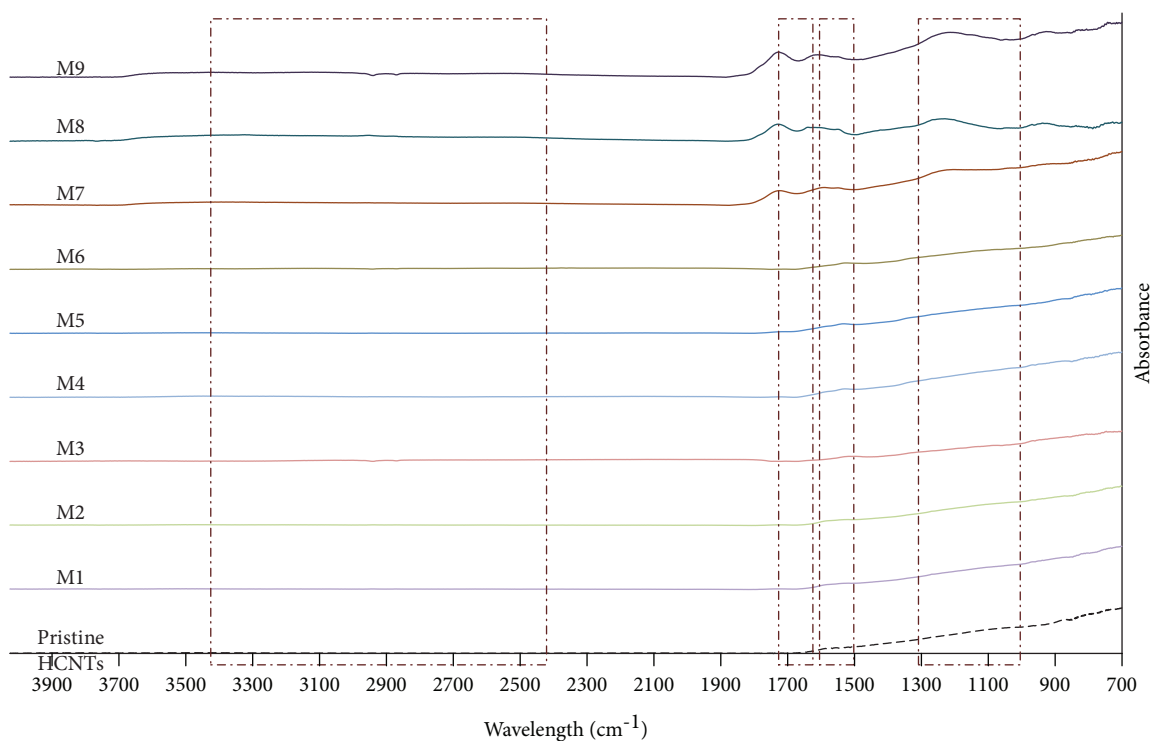


FIGURE 4: The FTIR spectra of the pristine and functionalized HCNTs and the four areas of interests (i.e., 1100-1300 cm^{-1} , 1500-1600 cm^{-1} , 1650-1730 cm^{-1} , and 2400-3400 cm^{-1}).

Figure 5 shows the XRD data for the pristine and the chemically functionalized HCNTs. The results revealed that all the chemically treated HCNTs had a reduction in their structural crystallinity (i.e., reduction of spectral intensity of

the peaks). However, the procedures that involved sonication with strong acidic solutions (i.e., procedures M7, M8, and M9 that uses acids with 16 M molarity) showed the largest reduction in crystallinity of the functionalized HCNTs. The value

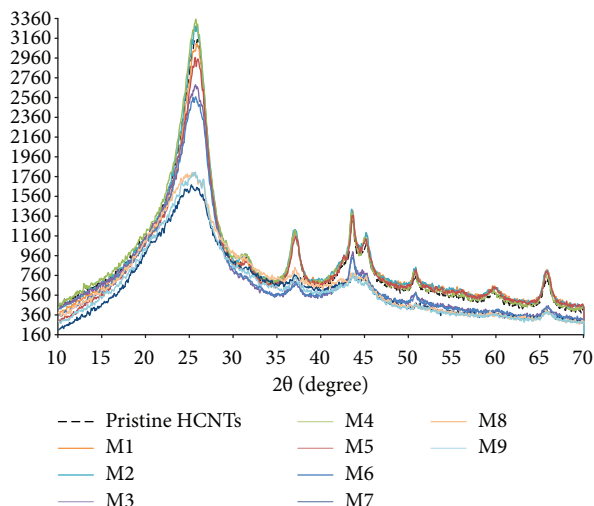


FIGURE 5: XRD data of the pristine and the chemically functionalized HCNTs.

reduction in peak intensity for these procedures (i.e., M7 through M9) was nearly 38%; higher reductions are considered to be undesirable to serve the main purpose of this study. It means that these chemically functionalized HCNTs cannot be as effective in providing considerable improvements in mechanical properties of polymeric nanocomposites. On the other hand, the chemical functionalization procedures M1 through M6 that demonstrated lower reductions in their peak intensities can be considered as more effective procedures for surface modification of HCNTs. These methods preserve the structural integrity of the HCNTs without generating severe damage to their structural crystallinity. As a result, procedures M1 through M6 can be considered more effective for chemical functionalization of HCNTs for structural nanocomposite applications. The resulting FHCNTs can be incorporated in polymeric resins and further investigated for their effectiveness as reinforcements in structural polymeric nanocomposites.

3.5. Scanning Electron Microscopy (SEM). The SEM images were primarily used to observe and compare the structural integrity and configurations of the helical CNTs before and after functionalization process. In addition, SEM was used for imaging and understanding the structure, length, diameter, and morphology of the HCNTs [52–55], as a nondestructive characterization tool [56]. Figure 6 shows the SEM images (i.e., in various magnifications) of the pristine HCNTs that were used in this study for chemical functionalization. The pristine HCNTs were measured 1–10 μm in length and 100–200 nm in diameter.

In this study, HCNTs were sonicated for different periods of time (i.e., 3, 6, and 9 hrs) in a mixture of sulfuric and nitric acid (i.e., with 3:1 mixing ratio) with different molarities (i.e., 3 M, 8 M, and 16 M). Figure 7 shows the SEM images (i.e., at $\times 15,000$ magnification) of the HCNTs after they were chemically functionalized using 9 different procedures (i.e., M1 through M9).

The comparison of the SEM images confirmed that the structure of HCNTs functionalized with M1 through M6 had gone through some minor alterations such as reduction in coil diameter, length, and shape. However, the HCNTs that were functionalized using stronger acids with 16 M molarity (i.e., procedures M7 through M9) were destroyed. This was consistent with the results that were obtained from both FTIR and XRD techniques.

These observations suggest that the use of harsher chemicals (i.e., high molarity acids) is not suitable for chemical functionalization of HCNTs that already include many periodic side-wall defects on their structures in forms of pentagonal and heptagonal rings. This explains that the use of strong acidic solutions can destroy the helical and graphitic structures of the HCNTs. It could be mentioned that the coil dimensions and configurations of these HCNTs may also influence the effectiveness of employed chemical functionalization methods. An interesting observation was made in the SEM image of method M4 (shown in Figure 7); here, a smaller-diameter HCNT was positioned inside a larger-diameter HCNT that could have been somewhat protected from the effects of acidic solutions. These concentric HCNTs can present very unique characteristics that could be utilized in nanoelectromechanical devices and sensors.

3.6. Effects of Acid Molarity. To investigate the effects of acid molarity on the effectiveness of chemical functionalization of HCNTs, three different acid molarities (i.e., 3 M, 8 M, and 16 M) were used in this study. Considering the visual dispersion test results (shown in Figure 2), no obvious differences were observed in dispersion uniformity and suspension stability of FHCNTs in DI water, except for the M3 samples that were sonicated with the lowest molarity acids (i.e., 3 M) for longest duration of time (i.e., 9 hours). It can also be mentioned that the use of stronger acids with more than 3 M molarities can increase the solubility/dispersion of the HCNTs. However, the Raman spectroscopy results (shown in Figure 3) demonstrated many discrepancies, and no clear correlation was observed to relate the changes in acid molarities to the variations of I_D/I_G values of the functionalized HCNTs. Regarding the XRD results (shown in Figure 4), the use of stronger acids showed higher reduction in structural crystallinity of the chemically functionalized HCNTs, as expected. Furthermore, comparison of the FTIR spectra of the chemically functionalized HCNTs with the pristine HCNTs (shown in Figure 5) showed changes in at least one of the four spectra regions. This could be an indication that the use of stronger acids can be more effective in surface modifications of HCNTs and attachments of functional groups on HCNTs surfaces.

3.7. Effects of Sonication Time. As mentioned before, in chemical functionalization methods M1, M2, and M3 the acid molarity was kept constant at 3 M while changing the sonication time from 3 to 9 hours in 3-hour increments (i.e., 3, 6, and 9 hours). Similarly, in methods M4, M5, and M6 the acid molarity was kept constant at 8 M, and in methods M7, M8, and M9 the acid molarity was highest and kept constant at 16 M while changing the sonication time

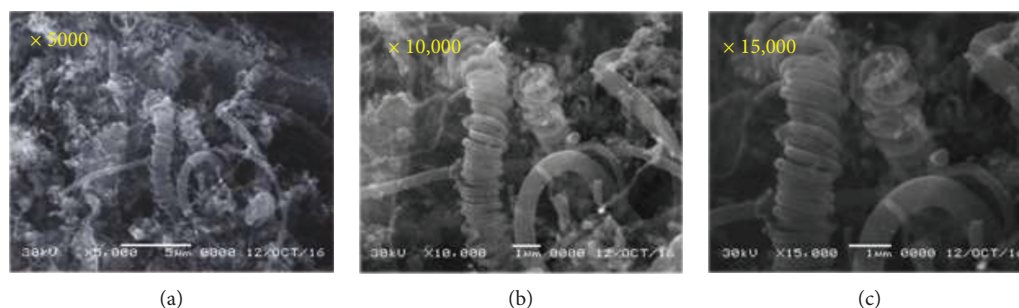


FIGURE 6: SEM images of pristine HCNTs with (a) 5000x, (b) 10000x, and (c) 15000x magnifications. The scale bars in these images are showing 5 μm , 1 μm , and 1 μm lengths, respectively.

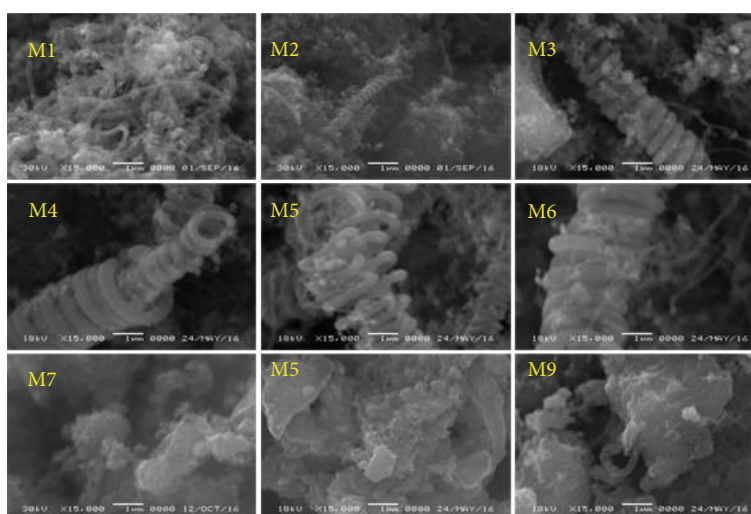


FIGURE 7: SEM images of the HCNTs that were chemically functionalized using M1 through M9 procedures. The scale bars in these SEM images are 1 μm long.

in the same manner. Overall, for most FHCNTs samples the dispersion uniformity and suspension stability were improved and the extension of sonication time from 3 hours to 9 hours was not very influential. However, the HCNTs that were sonicated for 9 hours in a weak acidic solution with 3 M molarity (i.e., procedure M3) showed opposite results and the FHCNTs were partially precipitated and showed poor suspension stability. In regard to Raman spectroscopy I_D/I_G ratios, prolonging the sonication time from 3 hours to 6 hours increased the I_D/I_G ratio of HCNTs treated with 3 M and 8 M molarity acids. However, the I_D/I_G ratio for the FHCNTs sonicated for 9 hours showed a reduction compared to the FHCNTs that were treated for 6 hours. For the HCNTs that were functionalized using strong 16 M molarity acids, prolonging the functionalization process reduced the crystallinity of HCNTs; however, a consistent pattern was not observed for the HCNTs that were functionalized with 3 M and 8 M molarity acids. The FTIR spectra revealed that by prolonging the sonication process, most of the treated HCNTs had a change in their FTIR spectrum compared to the processes involving a shorter period of sonication time. Overall, a specific and consistent pattern in variations of the characterization results could not be observed because

of the changes in sonication time. One possible reason could be the unique geometrical coil-shaped structures of HCNTs that increases their entanglements. Furthermore, the larger-diameter HCNTs that can potentially encapsulate the smaller-diameter HCNTs (see Figure 7) may act as a shield, thus reducing the functionalization effects.

It should be mentioned that the as-purchased HCNTs batches contain impurities in forms of amorphous carbon, ash contents, and catalysis particles (i.e., nearly 10% by weight). During the sonication with strong acids, the side-wall defects start forming on the HCNTs, while acids attack and dissolve the impurities. After 3 hours of sonication, the combination of the generated side-wall defects and the remaining impurities results in lower crystallinity measurements compared to the original crystallinity of the as-purchased HCNTs. As the functionalization process proceeded beyond 3 hours and reached 6 hours, more side-wall defects were generated; however, most of the impurities will be dissolved and removed from the HCNTs. As a result, the overall crystallinity of the functionalized HCNTs will be higher than that of the as-purchased HCNTs in the absence of impurities. Once the process of functionalization continues and reaches the 9-hour timeline, more side-wall

defects are generated on the structure of HCNTs reducing their crystallinity to less than that of the as-purchased pristine HCNTs. Therefore, considering the crystallinity of the HCNTs, 6-hour sonication time is the optimal processing time that can provide the highest crystallinity for HCNTs with minimal structural damage.

In this study, small amounts of helical CNTs (e.g., nearly 1 gram for each method) were functionalized, using the presented methods (i.e., M1 through M9). Our goal was to incorporate these functionalized HCNTs (i.e., at very low weight percentages of less than 0.1%) into polymeric resins for nanocomposite applications [57]. However, one can scale-up these chemical processes to functionalize higher amounts of helical CNTs (e.g., tens to hundreds of grams), using larger size containers, bigger sonication bath, bigger filters, and an appropriately designed fume hood system that can accommodate the larger size experimental setups. However, in a lab setting the washing and drying of the functionalized helical CNTs might take longer time periods and considerable amounts of helical CNTs might be lost during this step. These processes can be designed more precisely and engineered professionally for high yields.

4. Conclusion

Based on the characterization results presented in this manuscript, it was concluded that the sonication of HCNTs with a [3:1] mixture of sulfuric and nitric acid solution is an effective chemical route for covalent functionalization of HCNTs for nanocomposite applications. All chemically treated HCNTs samples demonstrated a higher dispersion uniformity and suspension stability, an increase in the Raman I_D/I_G ratio, and a change in the FTIR spectral compared to the pristine HCNTs samples, verifying our claim. Most of the treated HCNTs showed a reduction in crystallinity, which was consistent with our expectation that chemical functionalization using strong acids generates more side-wall defects on the structure of HCNTs, thus leading to a lower intensity of the graphitic peaks. The largest reduction in crystallinity was observed for samples that were treated with a strong 16M molarity acidic solution. Based on the SEM images and XRD results, using a very strong acidic solution (i.e., with 16M molarity) is not a suitable method for effective functionalization of HCNTs, without inducing substantial damages on their crystalline structures. These structural alterations could result in degradation of the mechanical properties of FHCNTs. For most treated HCNTs, the variations of acid molarities and sonication times were not very influential in further improvements of their dispersion uniformity and suspension stability; however, increasing the acid molarity from 3 M to 16 M was very effective, only for the HCNTs that were sonicated for 9 hours (i.e., M3, M6, and M9 HCNTs samples). Considering the XRD results, all functionalized HCNTs displayed a reduction in their structural crystallinity after using a stronger acidic solution. Overall, the chemical methods presented in this report could be used for effective functionalization of HCNTs for nanocomposite applications, except the ones that involved the use of harsher acidic solutions (i.e., M7,

M8, and M9 procedures which used 16 M molarity sulfuric and nitric acids). In conclusion, considering the results from visual dispersion tests, Raman spectroscopy, XRD, FTIR spectroscopy, and the SEM images of FHCNTs, functionalization methods M1, M2, M4, M5, and M6 are recommended for effective functionalization of HCNTs that could be used as reinforcement in polymeric nanocomposites. Among these recommended methods, M4 could be presented as the best method, since it requires weaker acids and a moderate sonication time. In a follow-up study, the authors have incorporated these FHCNTs in epoxy resin and fabricated nanocomposite samples for mechanical testing and further characterization that is currently under in progress.

Data Availability

The characterization data used to support the findings of this study are included within the article. Additional data are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

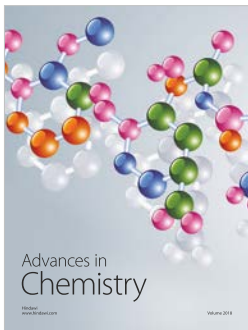
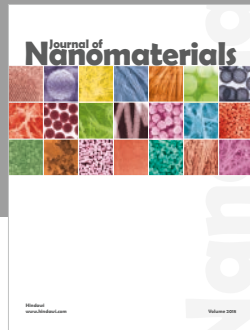
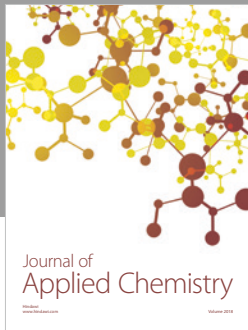
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