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Synthesis and Physical Properties Characterization of Montmorillonite-modified Carbon Nanotubes Filler

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Abstract. A combination of two different nano-sized materials could produce nano composite fillers. In this research, montmorillonite and carbon nanotubes were combined using sol gel method. Carbon nanotubes were oxidized in an acidic state and combined with montmorillonite at composition of 1:1. The fillers were subsequently characterized using FTIR, XRD and SEM to determine the physical properties of the synthesized material. The FTIR spectra of the montmorillonite-carbon nanotube nano filler display bands at 3429, 1076, and 798 cm⁻¹ which correspond to OH functional groups, Si-O-Si stretching, and Si-O-Si vibration, respectively. The unique diffractogram peaks of the montmorillonite-carbon nanotube nano filler at 2θ were 20.96, 26.59, 34.89, and 50.10°. Study of SEM images shows the growth of carbon nanotubes on the surface of montmorillonite. These filler properties lead to very promising requirement to be used in membrane fabrication.

Keywords: Filler, Sol-gel, montmorillonite, Carbon nanotube, FTIR, XRD, SEM.

1. Introduction

Montmorillonite (MMT) is an inorganic material that forms sheets consisting of tetrahedral and octahedral layer. Elements contain in the tetrahedral layer are Si, O, and H whereas the octahedral layer consists of Al, O and H [1]. These layers interact to form an electrostatic force. The crystal structure includes some empty spaces as well as Na⁺ and Ca⁺ ions [2] lead to general formula of molecules from this material becomes (Na,Ca)_{0.3}(Al,Mg)₂(Si₄O₁₀)(OH)_{2.n}H₂O. The octahedral layer contains iron and magnesium ions that located between two tetrahedral structures which contain silica and the excess of positive charge which compensated by the tetrahedral layer lacking of positive charge. These ions are isomorphic in the form of the tetrahedral layer where Si⁴⁺ ions are substituted by Al³⁺ and the octahedral layer where Al³⁺ ions are substituted by Mg²⁺ and Fe²⁺ [3].

The unique structure of MMT allows modification with organic and polymeric materials. The mixing of MMT with graphene is a route to obtain a modified, composite filler. The addition of filler to epoxy composites improved mechanical strength efficiently and thermal stability compared to pure epoxy composites [4]. Besides it being able to interact with polymers, MMT can also be used as an inorganic filler in polymer nanocomposite systems as MMT has a large ratio and surface area and naturally improve chemical stability and mechanical properties in the material [5].

Carbon nanotubes (CNTs) have nanostructures derived from graphene that are rolled up and have a variety of good chemical and physical properties. Carbon nanotubes are carbon allotropes that have a nanometer-sized diameter and micrometers in size (where the length for the diameter ratio exceeds 1000)



[6]. CNTs are cylindrical carbon structures with units and sizes in nanometers. CNTs are usually used for the manufacture of high-performance polymer composites due to their high flexibility, low mass density, large aspect ratio, and very high modulus and tensile strength [7]. These properties can be used as reinforcing materials and improve the mechanical properties of polymer nanocomposite [8]. Functionalization of CNTs walls is carried out using fluorination at a temperature of 150 to 600°C. This treatment can change the physical properties such as electrical conductivity, optical properties, and solubility, and increase chemical reactivity [9]. CNTs could be used as well as fillers by combined it with montmorillonite. The use of the composites on the membrane proved to increase the stability of the membrane [10]. In addition, carbon nanotubes are also reported as CNTs sulfonates which were applied to DMFC. The result shows that sulfonic acid-functionalised CNTs and fluorine-functionalised MMT have been effectively incorporated into the PVA matrix with sulfo-succinic acid as a crosslinked substance [11].

In this study, CNTs coated with MMT were isolated by the sol-gel method. This method was used to oxidize CNTs and mixed quantitatively with MMT.

2. Materials and Method

2.1. Materials

Materials/chemicals used in this work were multiwall carbon nanotubes (MWCNTs), sulfuric acid 18M, nitric acid 16M, distilled water, hydrochloric acid 12M, anhydrous ethanol, ammonium hydroxide, montmorillonite, and N,N-dimethylformamide.

2.2. Fabrication of nanocomposite filler

Fabrication were done by adding 1 gram of MWCNTs to a mixture of sulfuric acid 18 M and nitric acid 16 M (with a 3:1 volume ratio) and stirred for 6 hours at 100°C. The precipitate washed with distilled water until the pH of the filtrate was neutral and then filtered off. The precipitate then added with 100 mL hydrochloric acid 12 M and the mixture was stirred for 12 hours at 100°C. The product then filtered off and the solid was dried for 10 hours at 100°C. Next, the dry solid was added with a mixture of anhydrous ethanol, ammonium hydroxide and distilled water at ratio of 20:1:10 and stirred with ultrasonic for 0.5 hours. Subsequently, 1 gram of MMT was added quickly and the mixture was stirred for 12 hours at room temperature. After filtering it off, the precipitate was added with N,N-dimethylformamide, followed by ultrasonification for 0.25 hours. The product was filtered off and dried at 70°C.

2.3. Characterization

The filler was characterized using the Fourier Transform Infrared (FTIR) at 650-4000 cm^{-1} . X-ray diffraction analysis was carried out with Cu-K α radiation ($\lambda = 0.154056 \text{ \AA}$). Surface analysis using Scanning Electron Microscopy (SEM) was conducted to determine the morphological properties of fillers. The sample was prepared on the stub holder pin, coated by gold and using certain magnifications to get a clear surface image.

3. Results and Discussion

FTIR studies have been carried out to identify functional groups on the surface of MWCNTs. Figure 1 shows the FTIR results of pure MWCNTs, oxidised-multiwall carbon nanotubes (o-MWCNTs), MMT, and MMT o-MWCNTs. As observed in the MWCNTs sample, a typical signal at 1535 cm^{-1} shows the C=C vibration of structural aromatic. In addition, peak at 3421 cm^{-1} shows -OH from hydroxyl or carboxylic groups. Peaks at 2922 cm^{-1} attributed to C-H and at 1105 cm^{-1} is belong to C-O bond from ether or carboxylic acid groups. The wave number indicates the presence of a functional group of the sample on the surface of the MWCNTs.

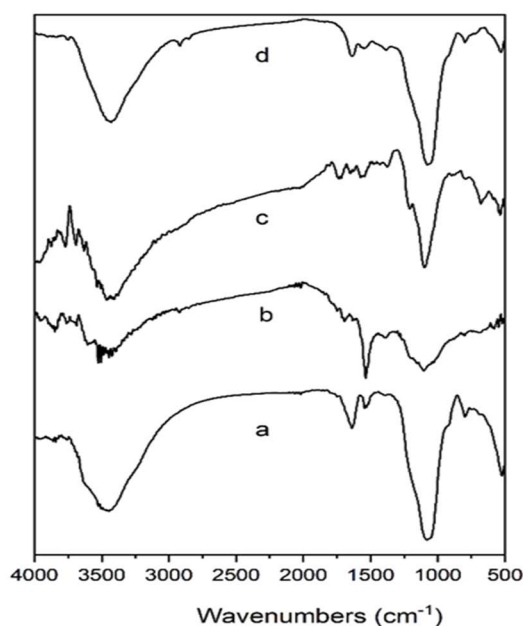


Figure 1. FTIR Spectra of MMT and CNTs (a) MMT (b) MWCNTs (c) o-MWCNTs (d) MMT-o-MWCNT

MWCNTs was oxidized using an acidic atmosphere. Oxidation of carbon nanotubes occurs at high temperatures and produces an opening part at the end of the structure. Consequently, the ends and or the side walls of this structure become more reactive [7]. The oxidizing agent activity produce various functional groups on the surface and this condition lead to polar group sticking at the surface of carbon nanotubes and results in changes in the nature of its hydrophobicity to be hydrophilic materials. The hydrophilic nature formed creates strong interactions with polymers. The results of the treatment shift the frequency and new peaks are formed. The increase in intensity occurred at 3414 cm^{-1} which shows -OH and 1099 cm^{-1} which indicates the presence of C-O bonds from ether groups. The new peak appears at 1735 cm^{-1} which indicates the presence of a C=O bond from carboxylic acid. The increase in wave number can be made possible when the sample is treated with a mixture of sulfuric acid and nitric acid. It is due to firstly the increase in oxygen content and secondly there is a correlation between the time of oxidation and the percentage of oxygen. In addition, samples also showed an increase in nitrogen percentage due to the ability of nitric acid to provide electrophilic nitronium ions capable of reducing aromatic rings [12]. Pure samples of montmorillonite show peaks at 3446, 1080, and 468 cm^{-1} which indicates OH stretching, Si-O stretching and at Si-O-Si bending, respectively.

Spectra of o-MWCNT and MMT mix nano fillers has also been depicted. The peak at 1076 cm^{-1} can be clearly observed because of the asymmetrical Si-O-Si stretch and peak at 798 cm^{-1} indicating the presence of asymmetric vibrations from Si-O-Si. In addition, there is a broad band at 3429 cm^{-1} attributed to the OH stretch. The results show that the multiwall surface of the carbon nanotube is effectively coated by montmorillonite. The hydrophilic properties of oxidized carbon nanotubes can create strong interactions with polymers lead to improve the mechanical and functional properties.

The X-ray diffraction pattern is shown in Figure 2. Pure samples of montmorillonite (a) have peaks at 2θ of 17.7° , 26.7° , 30.3° , and 45.4° . The pattern (b) show a certain number of diffraction peaks. Typical peaks of munti wall carbon nanotubes are 25.9° and 44.3° . After oxidation as depicted by (c), there was an increase in 2θ of 25.7° and a decrease in 2θ of 42.7° . Peaks after mixing between multiwall carbon nanotubes oxidized with montmorillonite (d) appears at 2θ of 20.9° , 26.6° , 34.9° , and 50.1° .

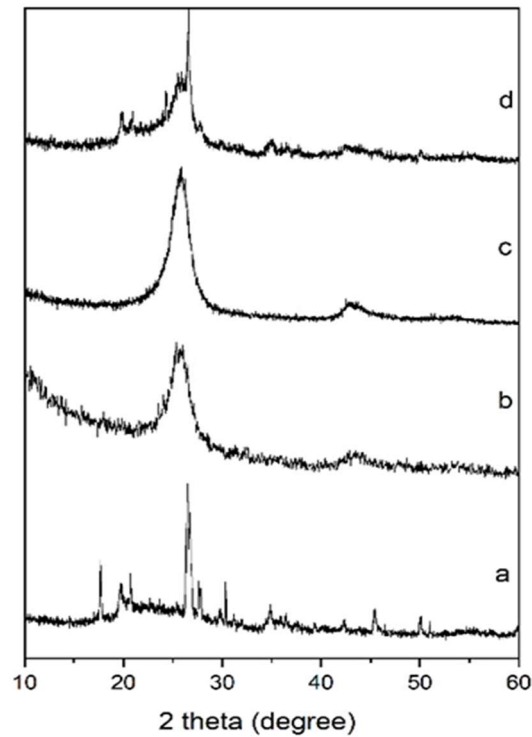


Figure 2. Diffractogram of MMT and CNTs (a) MMT (b) MWCNTs (c) o-MWCNTs (d) MMT-o-MWCNT.

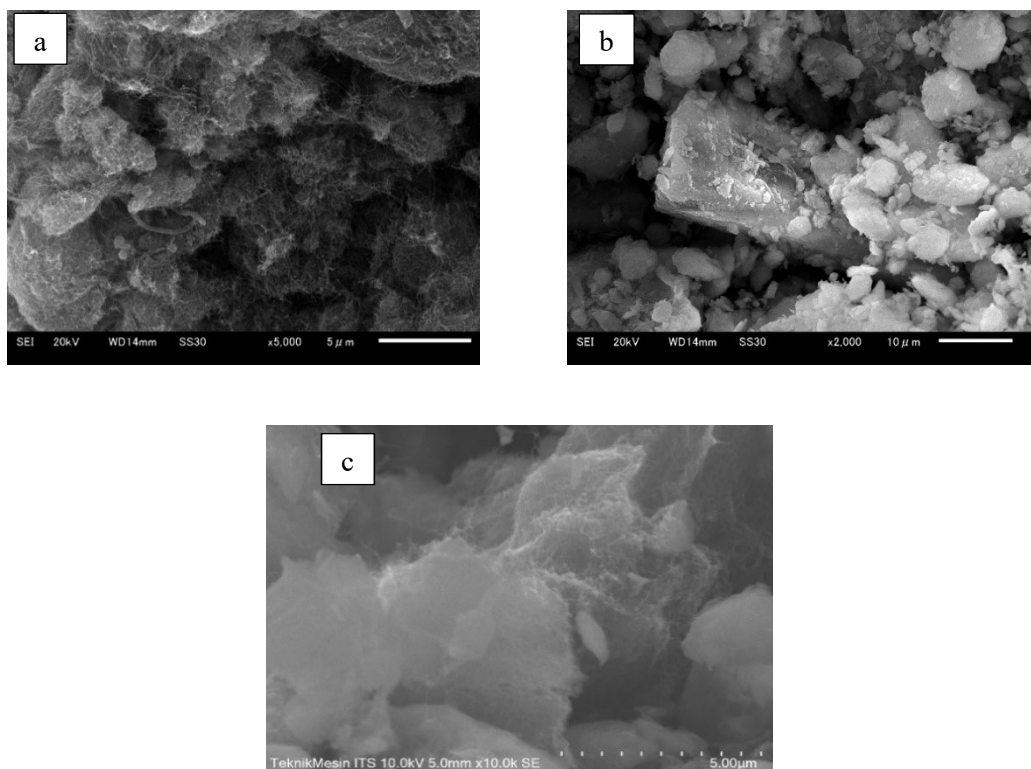


Figure 3. Surface morphology of (a) MWCNTs (b) MMT and (c) MMT-o-MWCNT

Morphological changes from the mixture of the two materials (composites) were detected clearly. The observation in Figure 3 shows the morphology of multiwall carbon nanotubes, montmorillonite, and a combination of multiwall carbon nanotubes with montmorillonite. The carbon is very small, homogeneous and forms tube-shaped. From the SEM picture, it can be seen that the size of the multiwall carbon nanotube (3a) is smaller than the size of montmorillonite, lead to the greater surface area of carbon nanotubes. Figure 3b shows the irregular and uneven surface of the montmorillonite and it is related to the surface of the montmorillonite layer that absorbs a large amount of multiwall carbon nanotubes shown in Figure 3c. The relationship between multiwall carbon nanotubes and montmorillonite can be clearly observed, and multiwall carbon nanotubes are distributed randomly on the surface of montmorillonite.

4. Conclusion

The nano-filler was synthesized by mixing two different materials using the sol-gel method. The filler has characteristic infrared frequencies of 3429, 1076, and 798 cm^{-1} and the XRD 2θ peak of 20.9, 26.6, 34.9, and 50.1°. The surface morphology of the nano-filler shows the strong physical bound between multiwall carbon nanotubes and the montmorillonite. These filler properties may lead to very promising requirement to be used in membrane fabrication.

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