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Preparation and Applicability of Vinyl Alcohol Group Containing Polymer/MWNT Nanocomposite Using a Simple Saponification Method

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1. Introduction

Polymer nanocomposites are increasingly desirable as coating, packaging, filtering and structural materials in a wide range of aerospace, automobiles, membrane, and electrical engineering applications [Mai and Yu, 2006; Ray and Bousmina, 2008]. This is due to our increased ability to analyze, synthesize, and manipulate a broad range of nanofillers and significant investment by laboratories and research centers in industry, government, and academia. In addition, polymers possess general advantages of low cost, lightweight, design flexibility, easy processing, and corrosion resistance. The polymer nanocomposites are one kind of composite materials comprising of nanometer-sized particles, typically at least one dimension less than 100 nm, which are uniformly dispersed in and fixed to a polymer matrix. In this way, the nanoparticles are acting like additives to enhance performance and thus are also termed nanofillers or nano-inclusions [Ramanathan et. al., 2007; Vaisman et. al. 2007]. The nanofillers can be plate-like, high aspect ratio nanotubes, and lower aspect ratio or equiaxed nanoparticles. Frequently employed inorganic nanofillers include metals and metal oxides, semiconductors, clay minerals, and carbon-based materials such like carbon blacks, carbon fibers, graphite and carbon nanotubes (CNTs).

CNTs have received much attention for their unique structural, mechanical, and electronic properties as well as their broad range of potential applications [Kim and Park, 2008; Kang et al. 2008; Xu et. al., 2008; Kumar, 2002; Wong et al., 1998]. CNTs are cylinder-shaped macromolecules with a radius as small as a few nanometers, which can be grown up to 20 cm in length [Zhu et. al., 2002]. Their properties depend on the atomic arrangement, chirality, diameter, and length of the tube and the overall morphology. They exist in one of two structural forms, single-walled carbon nanotube (SWNT) or multi-walled carbon nanotube (MWNT). SWNTs are best described as a 2-D graphene sheet rolled into a tube with pentagonal rings as end caps [Harris, 2004]. SWNTs have aspect ratios of 1000 or more and an approximate diameter of 1 nm. Similarly, MWNTs can be described as multiple

layers of concentric graphene cylinders also with pentagonal ring end caps. Conventional MWNT diameters range from 2-50 microns [Harris, 2004]. Measurements using in situ transmission electron microscopy and atomic force microscopy have produced estimates that Young's modulus of CNTs is approximately 1 TPa [Treacy et. al., 1996; Wong et. al. 1997]. For comparison, the stiffest conventional glass fibers have Young's modulus of approximately 70 GPa, while carbon fibers typically have modulus of about 800 GPa. CNTs can accommodate extreme deformations without fracturing and also have the extraordinary capability of returning to their original, straight, structure following deformation [Harris, 2004]. In addition, they are excellent electrical conductors and have very high thermal conductivities. Many of these exceptional properties can be best exploited by incorporating the nanotubes into polymer matrix, and the preparation of nanotube containing composite materials is now a rapidly growing subject.

Recently, our group has developed a process of simple saponification to make highly porous nanocomposites. In this process, at least one vinyl acetate (VAc) containing polymer or blend is dissolved in an appropriate solvent and a suitable viscosity of the solution is achieved. A functonalized nanotube was dispersed in polymer solution and then the polymer suspension was precipitated/saponified in alkaline non-solvent. This causes separation of the heterogeneous polymer suspension into a solid nanocomposite and liquid solvent phase. After rinsing off the coagulant and drying, sponge-like structure of connected matrix polymer and nanotube were obtained. Production parameters that affect the pore structure and properties include polymer and nanotube concentration, VAc content in polymer, saonification time and temperature, and precipitation media. These factors can be varied to produce porous structure with a large range of pore sizes, and altering chemical, thermal and mechanical properties. Porous materials are heterogeneous systems with complex micro-structure [Roberts and Knackstedt, 1996]. These systems are diphase composites with a solid matrix and gaseous filler [Mills et. al., 2003]. Physical and mechanical properties of such heterogeneous systems depend not only on the nature of the materials but on their morphology as well [Garboczi, 2000]. Materials with highly pore structure and controlled pore volume have potentials in a wide range of applications such as cell culture media, enzyme immobilization, organic electronics, membranes, absorbents, supports for liquid chromatography, ion-exchange applications, bio-separators, metal recovery and tissue engineering [Kanny et. al., 2002; Benson, 2003; Sears, et. al., 2010; Zeleniakiene, 2006]. It was the objective of the study reported here to use new approaches to produce vinyl alcohol (VOH) group containing polymer/MWNT nanocomposites with high porosity and to study their properties and applicability.

2. Preparation and properties of highly porous nanocomposites

Using CNTs as a property enhancing nanofiller for a high performance, lightweight composite is one of the lynchpins of nanocomposite research. The exceptional and unique properties of CNTs offer a great advantage for the production of improved composites. However, use of CNT reinforcements in polymer composites has been a challenge because of the difficulties in optimizing the processing conditions to achieve good dispersion and load transfer. Thus initial published results showed only modest improvement in mechanical properties with MWNT nanofillers [Thostenson and Chou, 2002]. One of the

major problems in the production of nanocomposites involving the use of nanofiller particles is the aggregation of the nanoparticles that severely limits the filler loading level. To improve dispersion, several techniques have been attempted, including the use of surfactants, sonication, and other mixing methods. Recent work has demonstrated superior dispersion of MWNTs in polymers by functionalization of the nanotubes to compatibilize them with solvents and the matrix polymers [Chiu and Chang, 2007; Wu et. al., 2006; Balasubramanian and Burghard, 2005; Yoon et. al., 2004]. The improved dispersion of nanotubes with functional groups has been accompanied by increased mechanical properties of the nanocomposite. Among of them, electron-beam irradiations are potent to induce the uniform and consistent modification of the MWNTs because of the high amount of energy, they impart to the atoms via the primary knock-on atom mechanism. This study investigated the preparation, properties and applicability of various VOH group conataing nanocomposites with high porosity through simple saponification method using electron-beam irradiated MWNT.

2.1 Functionalization of MWNT by electron-beam irradiation

CNTs are often formed in entangled ropes with 10–100 CNTs per bundle depending on the method of synthesis. They can be produced by a number of methods: direct-current arc discharge, laser ablation, thermal and plasma enhanced chemical vapour deposition (CVD) process [Lau and Hui, 2002]. The method of production affects the level of purity of the sample and whether SWNTs or MWNTs are formed. Impurities exist as catalysis particles, amorphous carbons and non-tubular fullerenes [Thostenson et. al., 2001]. Fig. 1 shows the SEM image and EDX analysis result of MWNT produced by a CVD process without any purification. As-received MWNT contain some impurities and entangle into a bulk piece. EDX results of the pristine MWNT show small peaks which are corresponding to Fe, Si and S. The Si peak has its origin in silicon substrate whereas the other peaks are due to the precursor gases present in the gas mixture and catalyst. The Pt peaks was due to the platinum sputtering process during SEM sample preparation. Average diameter and average length of MWNT were 15 nm and 20 μm, respectively.

The MWNT were electron-beam irradiated in air at room temperature using an electron-beam accelerator. Irradiation dose of 800, 1000, and 1200 kGy were used, respectively. Fig. 2. demonstrates a higher magnification SEM micrographs of MWNT before and after
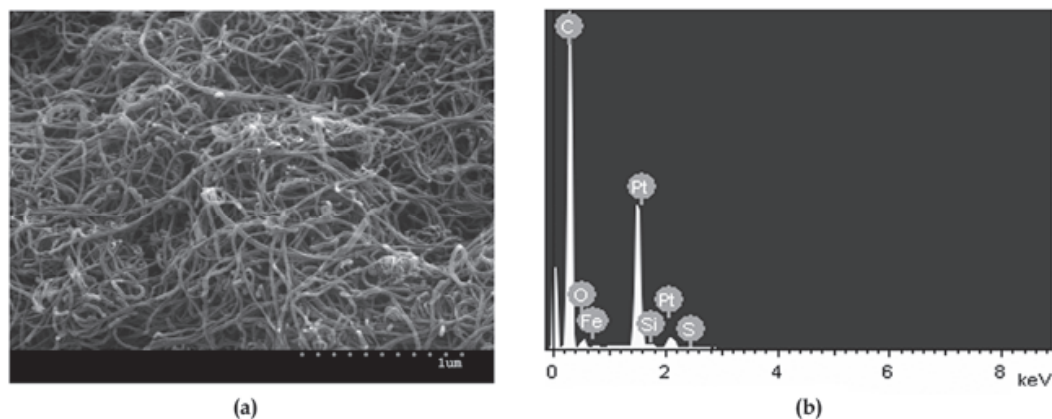

(a)   (b)

Fig. 1. SEM image and EDX analysis result of the pristine MWNT
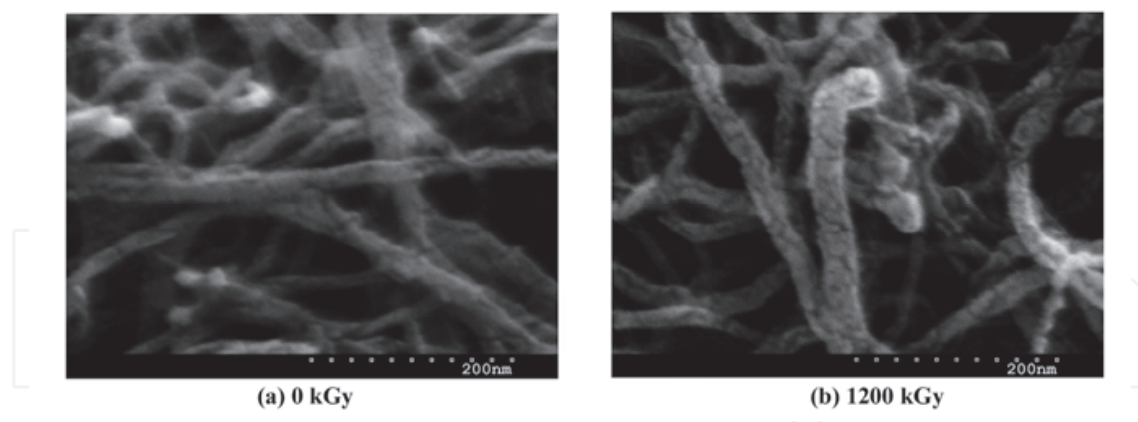
(a) 0 kGy   (b) 1200 kGy

Fig. 2. SEM micrographs of the surface morphology of pristin MWNT and MWNT1200

treatment with the electron-beam irradiation. The pristine MWNT has relatively smooth surface without extra phase or stain attached on its sidewall. Although the electron-beam irradiation increased up to 1000 kGy, the surface appearance did not changed compare to the pristine MWNT. After the 1200 kGy EB irradiation, the smooth surface was disappeared, many wrinkled structure were formed, and the surface roughness increased. In general, the surface of the synthesized CNT is smooth and relatively defects free. However, stresses can induce Stone Wales transformations, resulting in the formation of heptagons and concave areas of deformation on the nanotubes [Thostenson et. al., 2001].
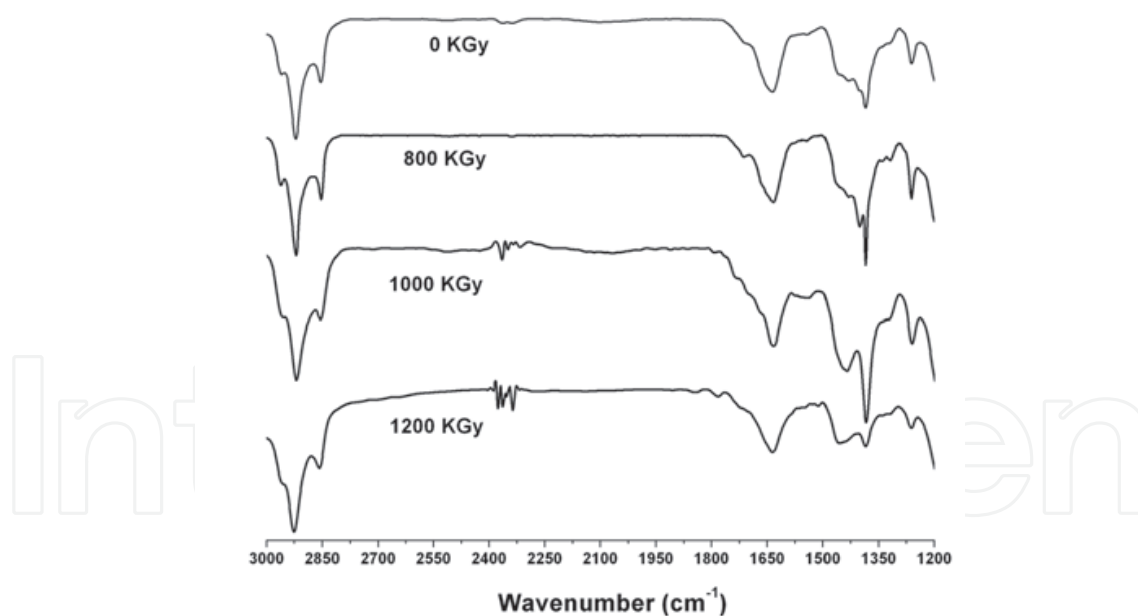

Fig. 3. FTIR spectra of the electron-beam irradiated MWNT

The pristine MWNT and electron-beam irradiated MWNT were further characterized by FTIR spectroscopy. The pristine MWNT exhibit the peaks of C-C bond stretching appeared in the range of 3000–2800 cm^{-1}. FTIR spectra of MWNT after electron-beam irradiation more than 1000 kGy showed new peaks at 1782 cm^{-1} due to the C=O bond resulting from C=O stretch of the carboxyl and carbonyl groups (Fig. 3). Element analysis presented a decrease in the hydrogen/carbon ratio up to 1000 kGy. After the 1200 kGy irradiation, the hydrogen

/carbon ratio was significantly increased. This indicated that low irradiation dose clean the impurities of MWNT, but the increase of irradiation doses could affect surface roughness and chemical composition.

2.2 Preparation of porous VOH group containing polymer/MWNT nanocomposites

Highly porous VOH group containing polymer nanocomposite particles were created by simple saponification method. A VAc group containing polymer/MWNT/toluene suspension was saponification by dropwise addition to KOH in alcohol solution which saponifying the VAc groups in polymer selectively. The VAc group containing polymer used in this study was poly(ethylene-*co*-vinyl acetate) (EVA, VAc content 28 and 40 wt%) and poly(vinyl acetate) (PVAc). The heterogeneous suspension was stirred at room temperature for ambient time, and then the solution was filtrated, and washed with methanol. The approximate size of the prepared particles is 30-50 µm. The abbreviation of the sample name, EVA40/MWNT1200, for example, means that the content of VAc in the EVA was 40 wt % and MWNT was electron-beam irradiated 1200 kGy does.
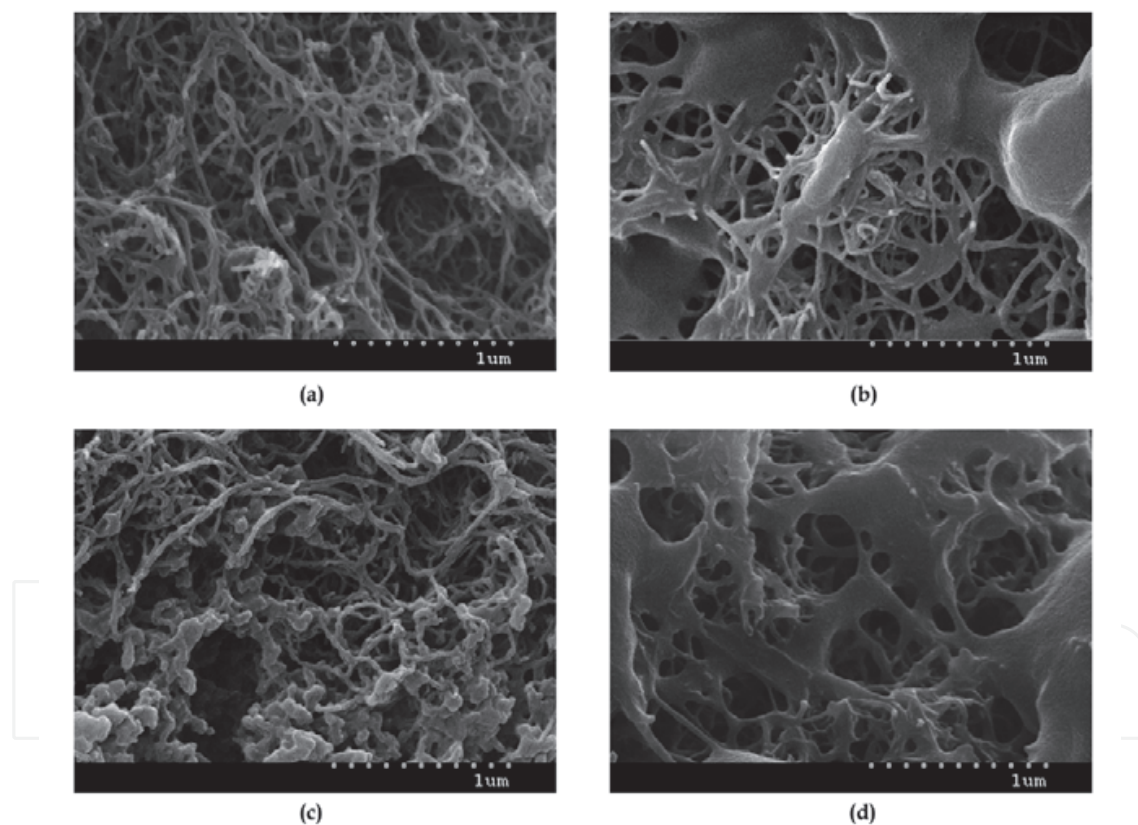

Fig. 4. SEM micrographs of the 3h-saponified PVAc/MWNT1200 (a: ethanol/KOH, c: methanol/KOH), EVA40/MWNT1200 (b: ethanol/KOH) and EVA28/MWNT1200 (d: ethanol/ KOH) coagulants

After rinsing off the coagulant and drying, sponge-like structure of connected matrix polymer and MWNT were obtained. This causes separation of the heterogeneous polymer suspension into a solid nanocomposite and liquid solvent phase. The precipitated coagulants form a porous structure containing a network of uniform open pores. Production

parameters that affect the pore structure and properties significantly include the MWNT concentration, the VAc content in polymer, the precipitation media and the saonification time. At low polymer/MWNT suspension concentrations, the particles were less porous and the precipitated polymer phase had a granular structure consisting of aggregates of precipitated polymer micelles. While at high concentrations, void porosity was increased and the precipitated polymer phase became a spongy-like structure. It was also found that as the VAc content in polymer was decreased, the average pore size increased and number was decreased. In sharp contrast, the irradiation does of MWNT was not affected in pore size and structure. The pore size was obtained directly by image analysis from higher magnification SEM micrographs. Pore size control can be achieved with sub-nanometer 10 to 200 nm range by selecting the matrix materials and the saponification conditions
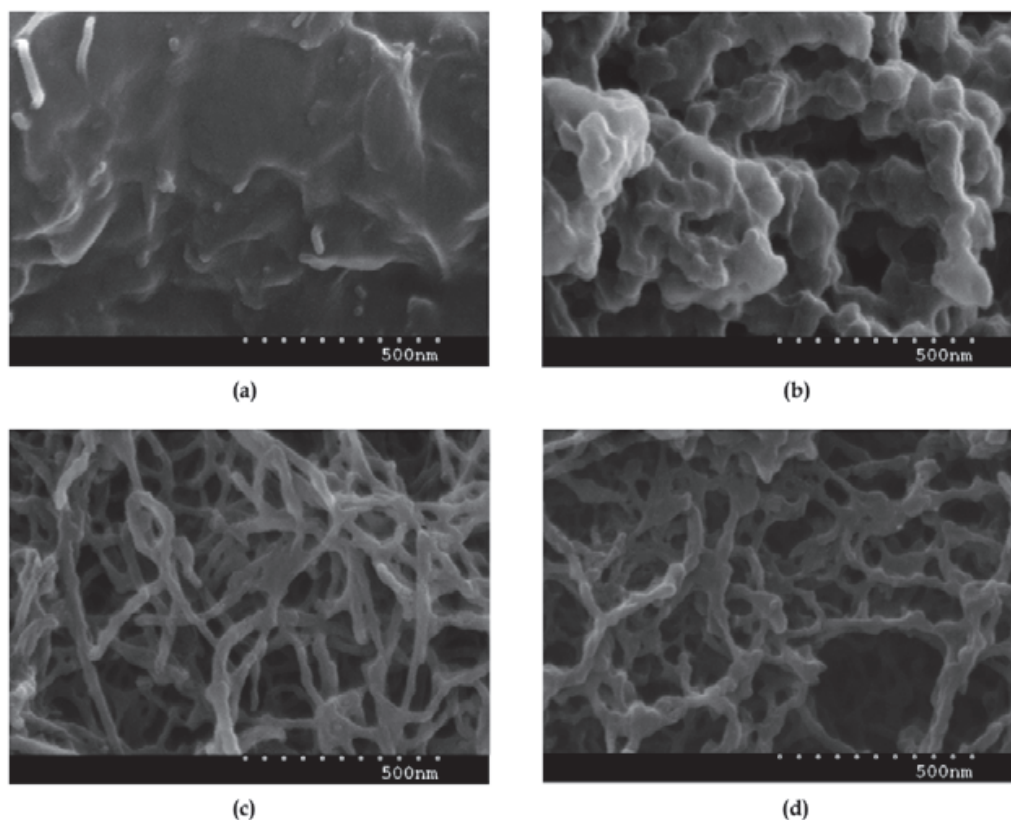

Fig. 5. SEM micrographs of the saponified PVAc/MWNT1200 in methanol/KOH along with that of its corresponding saponification time [(a) precipitated in hexane, (b) 1 h, (c) 3 h, and (d) 6 h]

Fig. 5 represents the SEM image of PVAc/MWNT1200 coagulant surface prepared using methanol/KOH solution as the saponification time. The surface of the PVAc/MWNT1200 coagulant shows a dense skin layer, which appears to be nonporous. The formation of the skin layer and lack of an interconnected pore structure is likely due to the rapid precipitation where the rate of inter-diffusion depends on the value of the solubility parameters of the solvent and non-solvent. As the saponification time increase, the PVAc/MWNT1200 nanocomposite coagulant form a porous structure containing a network of open-cell pores at the nanometer length scale.

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2.3 Mechanical properties of EVOH/MWNT nanocomposites

Table 1 demonstrates the tensile properties of the electron-beam irradiated MWNT (MWNT1200) filled EVA nanocomposites before and after saponification in KOH/metanol solutuion. PVAc/MWNT1200/toluene and EVA/MWNT1200/toluene suspensions were prepared with MWNT1200 loadings of 10 wt%. The suspensions were solvent-casting onto a PTFE film-supporting surface and the prepared film was subsequently hot pressed to sheet of uniform thickness. Dumbbell specimens for tensile tests were prepared in accordance with IEC 60811-1-1 specification. Tensile properties of samples were determined with a universal test machine. The hot-pressed sheets of PVAc/MWNT-10% nanocomposite are very brittle and can not be perform the tensile test.

Sample code	Tensile properties	
	Tensile strength (MPa)	Elongation at break (%)
EVA28	10.6 ± 0.9	1472 ± 106
EVA28/MWNT1200-10%	8.9 ± 0.8	162 ± 20
EVA28/MWNT1200-10%-6h	17.6 ± 2.0	412 ± 50
EVA40	9.0 ± 1.0	1625 ± 156
EVA40/MWNT1200-10%	7.2 ± 0.9	522 ± 59
EVA40/MWNT1200-10%-6h	18.7 ± 2.3	756 ± 81

Table 1. Tensile properties of the hot-pressed specimens

As shown Table 1, addition of 10 wt% of MWNT1200 reduced the tensile strength of EVA28 and EVA40 by 16 and 20 %, respectively. This means that MWNT1200 contents were at values of 10 wt%, the MWNT did not disperse uniformly and they formed agglomerations in the polymer matrix. In addition the elongation at break of both nanocomposites decreased with the presence of filler that indicates interference by the filler in the mobility or deformability of the matrix. It is noteworthy that tensile strength and elongation at break of nanocomposite samples prepared by simple saponification method were significantly increased than those of corresponding unsponified ones. After 6h saponification time, the tensile strength of EVA28/MWNT1200-10% and EVA40/MWNT1200-10% was increased by about 98 and 160 %, respectively. This is indicated that saponification process enhances the overall dispersion state of the MWNT nanofibers due to enhanced interactions between the filler and the polymer matrix.

2.4 Resistivity of saponified VAc containing polymer/MWNT nanocomposites

The surface electrical resistance of the hot-pressed films (80 mm length × 10 mm width) was detected by a megohmmeter according to ASTM D 257. The charge time was 10 s, and the current stress of the measurements was 5000 V at 20 ± 1 °C. Volume resistivity (ρ_v) of prepared films was calculated by use of equation (1).

$$\rho_V = \frac{AR_V}{L} \qquad (1)$$

Where A, R_v and L represent the area of the effective electrode (cm²), measured resistance (Ω), and distance between electrodes (cm), respectively.

Fig. 6 show a rapid decrease in ρ_v of PVAc/MWNT1200, EVA40/MWNT1200, EVA28/MWNT1200 nanocomposites with increasing MWNT content. This rapid decrease is characteristic of the loading level at which the MWNT particles begin to come into contact with one another to form a electroconductive network. As MWNT particles are loaded in a polymer matrix over a percolation threshold concentration, the nanocomposite becomes an electrical conductor at room temperature. The percolation threshold of the PVAc/ MWNT1200, EVA28/MWNT1200, and EVA40/MWNT1200 nanocomposites formed by solution mixing was approximately 2.5, 2.5 and 5 wt%, respectively due to the advantageous effect of composites with higher aspect ratios compared with spherical or elliptical fillers in forming conducting networks in the polymer matrix.
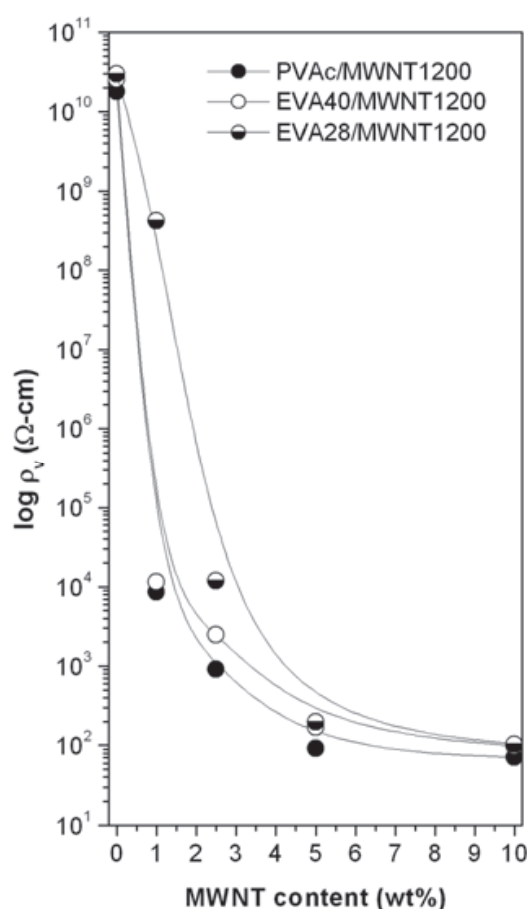

Fig. 6. ρ_v change of the PVAc/MWNT1200, EVA40/MWNT1200 and EVA28/MWNT1200 nanocomposites with increasing MWNT content

The electron transport in CNT assemblies is different from that in individual nanotubes. It has been reported that SWNT fibers exhibit room temperature resistivity in the range of 1 ×10^{-4} to 7×10^{-4} Ω-cm, which is nearly 100 times higher than that of single CNT. The resistivity of MWNT fibers are one or two orders of magnitude higher than that of SWNT fibers [Zhang et. al., 2004; Zhu et. al, 2006]. Such large differences between single nanotubes and fiber assemblies may arise from high impurity content such as amorphous carbon and catalytic particles in the fibers, which may profoundly affect electron transport by causing significant scattering, and contact resistances between nanotubes [Li, 2007]. Therefore, two

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approaches can be used to improve the electrical conductivity of polymer/CNT nanocomposites: 1) reduce the impurity content of CNTs by post treatments [Li, 2007]; 2) minimize the contact distances between nanotubes by enhancing the dispersity of individual nanotubes.

Fig. 7 shows the dependence of ρ_v change for PVAc/MWNT1200, EVA40/MWNT1200 and EVA28/MWNT1200 nanocomposite films with the saponification time. Among them, PVAc/MWNT1200 nanocomposite showed lowest ρ_v and it has also the lowest ρ_v after saponification process. It can be also founded that the ρ_v almost maintained with saponification time. This may be because of the easy dispersion of MWNT particles in the rubbery phase and hence the high VAc polymers disperse the fillers well. The EVA28 and EVA40 consists of more crystalline phase and hence the MWNT particles find it more difficult to disperse and hence form relatively more agglomerations, whereas in high VAc grades, the amount of free volume is more and hence the fillers can disperse relatively easily [George and Bhowmick, 2009]. In sharp contrast, the ρ_v of saponified EVA40/MWNT1200 and EVA28/MWNT1200 nanocomposites decreased significantly with the saponification time. An increase of VOH units would raise the intermolecular interaction between EVOH molecules, and it enhanced crystallization of EVOH molecules. When the matrix polymer crystallinity increased, filler particles segregate to the non-crystalline interlamellar and interspherulitic regions and forms more inter-connective pathways, which results in lowering the resistivity [Lee et. al., 2011].
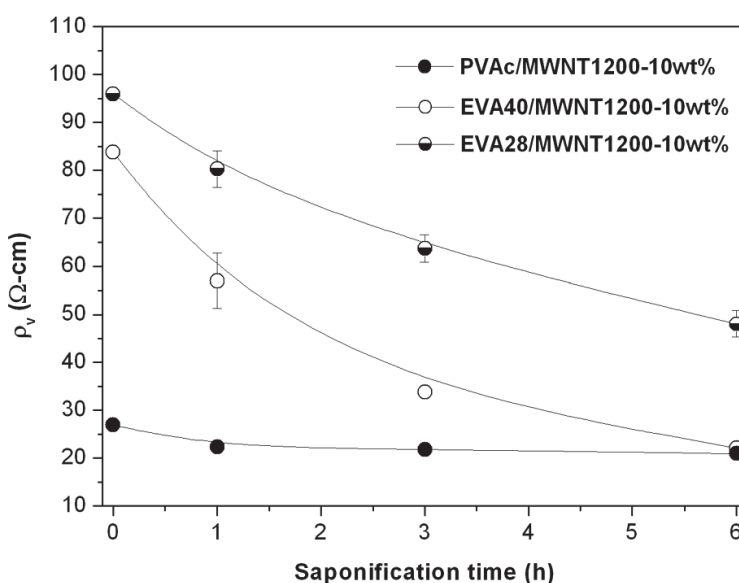

Fig. 7. ρ_v change of PVAc/MWNT1200, EVA40/MWNT1200 and EVA28/MWNT1200 nanocomposite powders with saponification time

In fact, this can be confirmed from XRD spectra of EVA28 in Fig. 8. On curve, there is a strong diffraction peak at $2\theta=20.8°$ and a weak diffraction peak at $2\theta=5.8°$. These diffraction peaks attribute to the crystallization of the main chain. Both the relative intensity increment and the peak shift at higher 2θ with the saponification time is a strong indication of the increased crystallinity of the saponified samples relative to the pure EVA28. All the observations are in accordance with the tensile properties discussed above.
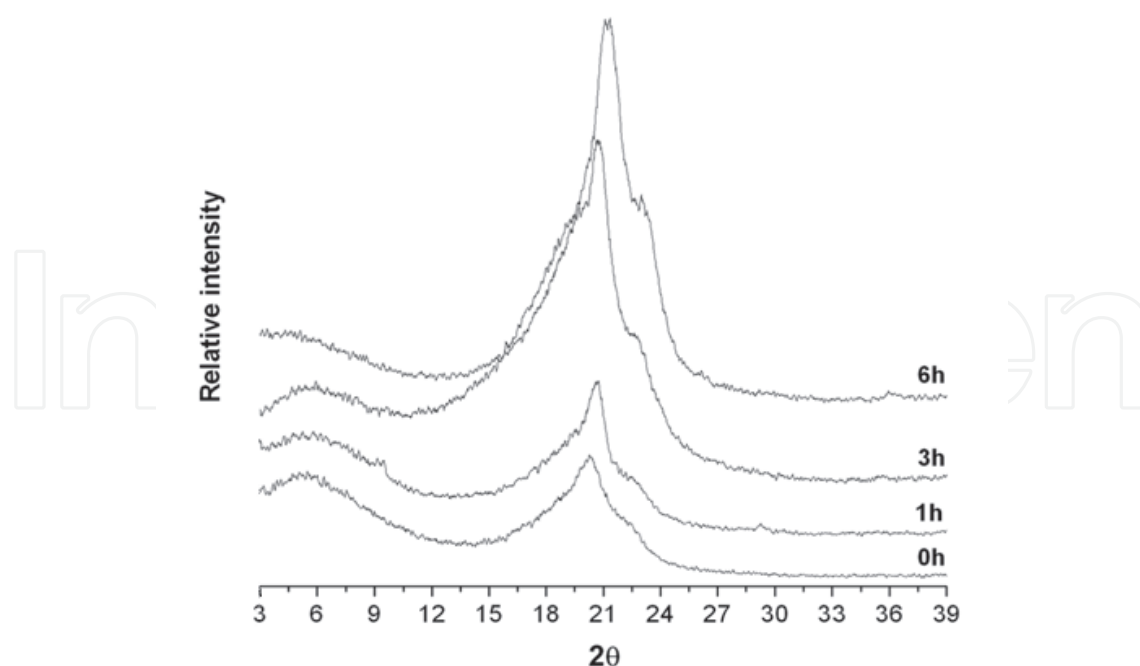
Fig. 8. XRD spectra of the saponified EVA28 along with that of its corresponding saponification time

3 Applicability of VOH group containing polymer/MWNT nanocomposites

3.1 Positive temperature coefficient (PTC) heating elements

Electroconductive polymer nanocomposites are becoming increasingly useful because of their unique combination of metallic electroconductivity and polymer properties. Currently, there are several methods that can be used to impart electroconductivity to polymers: doping of intrinsically electroconductive polymers, incorporation of electroconductive additives into an insulating polymer matrix and coating of fibers with metals or electroconductive chemicals. Applicability of VOH group containing polymer/MWNT nanocomposites can be used in a variety of industrial applications such as heating elements, temperature sensors and current limiters [Kim and Park, 2008; Park et. al., 2004; Park et. al., 2005; Park, 2005; Park, 2006]. This is mainly due to their positive temperature coefficient (PTC) of resistivity. It has been well accepted that the strong PTC effect of them is caused by an increase in the average inter particle distance of filler, which is created by the large thermal expansion that occurs as a result of the melting of the polymer crystals [Park et. al., 2003].

Fig. 9 indicates resistivity-temperature behavior of the saponified EVA28/MWNT-10wt% nanocomposites. All nanocomposites exhibited both negative temperature coefficient (NTC) and PTC effect. A NTC indicates that resistivity decreases with temperature; a PTC indicates that resistance increases with temperature. However, this NTC effect could be eliminated easily by chemical or electron-bam radiation crosslinking. As the saponification time increased, the PTC maximum peak temperature of nanocomposites is shifted at higher temperatures. A reproducible PTC composite should have high PTC effect to prevent the composite from overheating and relatively low room temperature resistivity to ensure sufficient thermal output. From Fig. 9, 3h- and 6h-saponified nanocomposites showed good PTC behavior with high melting temperature. They have great potential for use in industrial applications such like PTC heating elements and coating materials for surface film heater.
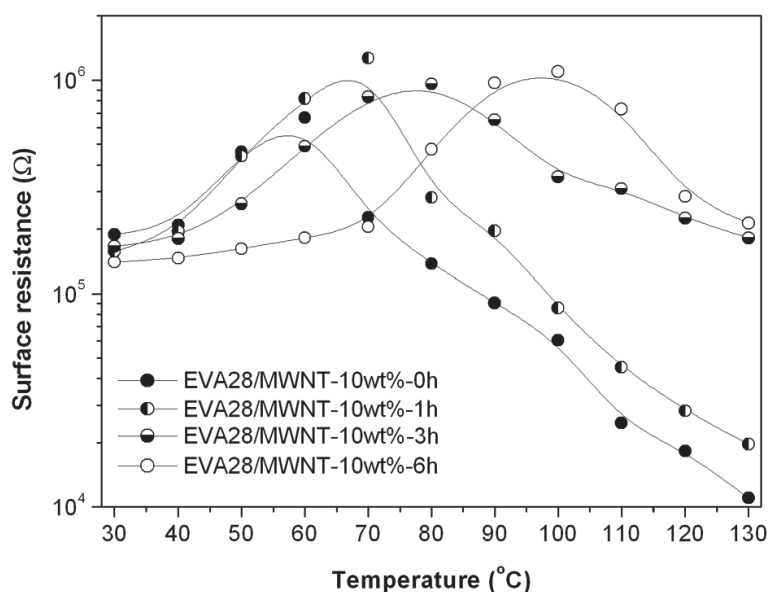
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Fig. 9. PTC peak temperature change of the EVA28/MWNT-10wt% nanocomposites with saponification time

3.2 Electromagnetic interference (EMI) shielding materials

As electromagnetic radiation, particularly that at high frequencies tend to interfere with electronics, EMI shielding of both electronics and radiation source is needed and is increasingly required by governments around the world [Chung, 2001]. The radiation may be either electromagnetic in nature, such as X-rays and gamma rays, or charged particles, such as beta particles and electrons. The lifetime and efficiency of them can be increased by the effective shielding. Generally, highly electroconductive materials such like metals are used for shielding application. However, metals have their own shortcomings like heavy weight, susceptibility to corrosion, wear, and physical rigidity [Wu et al., 2006]. The polymer nanocomposites filled with carbon materials are attractive for EMI shielding materials which helps to reduce or eliminate the seams in the housing that is the shield. Many researches have been conducted to improve the EMI shielding of polymer materials by coating an electroconductive layer on the surface, incorporating electroconductive fillers, or utilizing electroconductive polymers. Among various electroconductive fillers that have been utilized, CNT is one of the most promising candidates, not only because of its good electrical conductivity but also because of its ability to improve mechanical properties. Recently, the mass production of MWNT causes price reduction. The MWNT is more affordable for EMI shielding material application in nanocomposites [Wu et. al., 2006].

3.3 Antibacterial agents

In our previously study [Lee et. al., 2011], it is curious to observe that saponified EVA had some antimicrobial activity against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*). Antibacterial activity of EVA28 powders was gradually increased with saponification time. 6h-saponified EVA extirpated 45 and 57% of the viable cells of *S. aureus and E. coil*, respectively. As shown in Fig. 10, it possesses a porous structure that can adsorb various ions and organic molecules easily in its pores and on its surfaces. Bacterial growth or

movement may be restricted by porous media physical conditions. Bacteria are small living organism; their length change between 0.5-10 µm and their diameters are between 0.2-10 µm. Porosity networks with pore throat sizes narrower than the bacterial cell diameter prevent bacterial penetration into these regions [Fredrickson et al., 1997]. Porous regions are diffusion-limited or that are experiencing biomass sloughing due to rapid flow-induced shear forces [Applegate and Bryers, 1991] may be less likely to harbour significant bacterial populations. Furthermore, CNTs have been recently demonstrated to possess antimicrobial properties, and their relevant activities were ascribed to the behaviour of 'nanodart' with the proposed physical damage mechanism [Kang et. al., 2008].
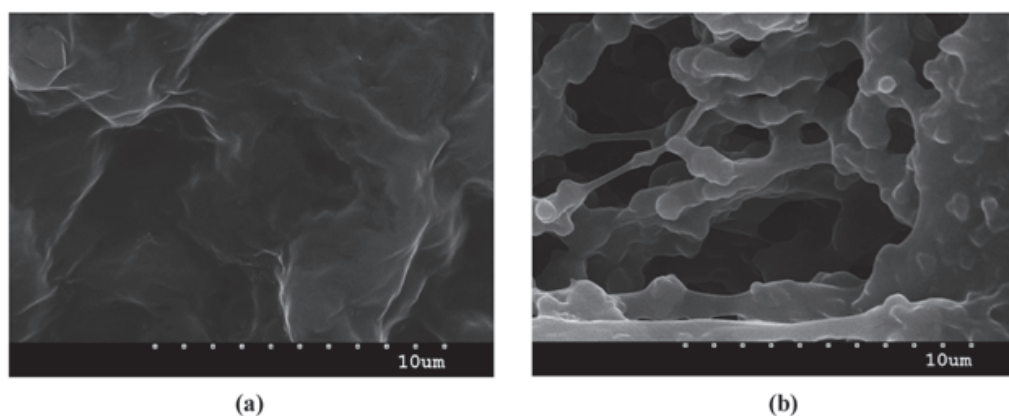

Fig. 10. SEM micrographs of the EVA28 (a) and 6h-saponified EVA28 (b) in ethanol/KOH solution

3.4 Membrane for purification and separation

The development of advanced membrane technologies with controlled and novel pore architectures is important for the achievement of more efficient and cost effective purification. Present polymeric membranes are well known to suffer from a trade off between selectivity and permeability, and in some cases are also susceptible to fouling or exhibit low chemical resistance [Sears, et. al., 2010]. Due to the simplicity of their preparation, Bucky-papers were one of the first macroscopic structures fabricated from CNTs [Baughman et. al., 1999; Kim et. al., 2006]. The Bucky-paper is used to describe a mat of randomly entangled CNTs prepared by filtration [Kim et. al., 2006; Endo et. al., 2003] or alternative papermaking processes. CNTs are known to have a strong tendency to aggregate due to van der Waals interactions, and it is these van der Waals interactions which also hold the CNTs together into a cohesive Bucky-paper. Longer, narrower and more pure CNTs typically lead to stronger Bucky-papers with higher tensile strengths. With increasing MWNT diameter, the attractive van der Waals forces between CNTs become less effective, leading to Bucky-papers with lower tensile strength and poor cohesiveness. This can be improved to some extent through functionalization of MWNTs or the addition of polymers [Xu et. al., 2008]. Recently, EVOH membranes have attracted plenty of research interest in fields of biomedical science and water treatment because of its good blood compatibility and hydrophilicity [Guerra et. al. 1995; Young et. al., 1997]. As noted in the previous section, highly porous EVOH/MWNT nanocomposites with higher tensile strength were easily prepared by simple saponification method. As such they are of interest for applications such

like direct contact membrane distillation, capacitive deionization, and filtration of particles including bacteria and viruses.

3.5 Carriers of catalyst and functional materials

The highly porous nature of materials enables their use as carriers [Benson, 2003]. High surface area and controlled pore size distribution available as the raw material to the shape or monolith forming process. Capillary forces are quite strong, and will tightly contain many substances for slow release. In some cases, an encapsulation step may be required to ensure long term retention of contained substances. In one experiment, an accelerator component was placed into highly porous spheres, retained, and premixed with an adhesive. The two parts were mixed without fear of reaction since capillary forces prevented viscous liquids from escaping. Later, the reaction was initiated when the beads were crushed or heated to the activation temperature [Benson, 2003]. In addition any catalytic material attached to highly porous nanocomposite surfaces would have more efficient interaction with reactants due to large cavities and interconnected pores. As a main constituent for carrier materials provide a controlled surface area and porosity for the final catalytic system. This unique structure permits reactants to flow into spheres, interact with catalysts, form products, and still allows room for products to flow out and away from newly arriving reactants. Such accessibility of the catalyst to reactants is important for rapid and efficient reactions. Carboxyl groups and other functional groups could be modified on the MWNT surface [Chiu and Chang, 2007].

3.6 Chromatography and bio-processing

Large interconnected cavities contained within chemically stable EVOH containing polymer/MWNT nanocomposites are ideally suited for liquid chromatography applications, including bio-processing. Because cavities of them are relatively uniform and are individually connected through a network of smaller pores, sample molecules find clear ingress and egress through the matrix, and diffusion limitations characteristic of conventional porous polymers are absent [Benson, 2003]. Therefore, mass transfer characteristics are extremely attractive. The focus of bio-processing is using living cells to make desired products, which is commonly carried out in a bioreactor. Downstream processing from this reactor gives concentrated and purified products. Separation of proteins and other biopolymers on conventional porous polymers occurs only in the outside few angstroms of the spheres [Krijgsman, 1992]. In contrast, because of the interconnections, separation on porous MWNT nanocomposites occurs throughout the entire volume of particles. Furthermore, since there are no needs to be modified by coating the surface with a hydrophillic polymer to avoid low recovery, pressure drop through columns of these particles is extremely low. In addition, the synthetic polymer-based media is their resistance to extreme chemical conditions, such as pH. These properties, and the suitability of such structures for containment and separation of biopolymers, make them ideal candidates for bio-processing applications.

3.7 Polymeric fillers

Surface modification of filler is an important topic. Fillers are commonly incorporated into polymeric resin compositions in order to modify the properties of the resin. However, most inorganic fillers have a naturally hydrophilic surface which is therefore not easily wetted by

polymeric resin compositions which are generally hydrophobic. This problem is especially acute when the resin is in the form of a low-viscosity liquid because under these conditions it is difficult to dissipate sufficient energy in the composition by mechanical agitation to effect dispersion of the inorganic filler in the polymeric resin. A further disadvantage of conventional inorganic fillers is that they generally have associated with them a small, but significant, quantity of water. EVOH copolymers have been widely used as food packages, biomedical and pharmaceutical industries due to their excellent gas barrier properties, high resistance to oils, good mechanical strength and harmlessness to health [Okaya and Ikari, 1992]. They also have significant potential for polymeric filler and inorganic filler surface modifier due to their combined effect of hydrophilicity, as a consequence of the -OH side groups. Since the materials prepared by this method for industrial applications such like polymeric filler in electro-conductive and electrostatic discharge composite systems, polymer compound systems, and aqueous coating systems.
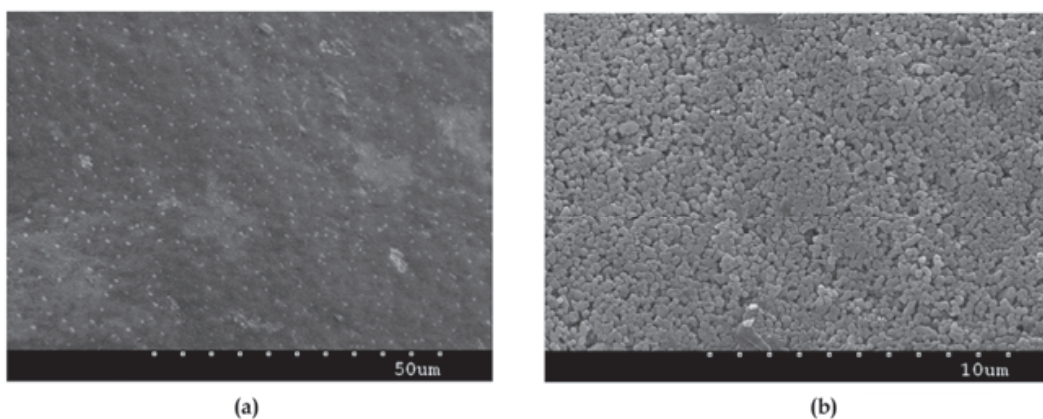

Fig. 11. SEM image of the EVOH/MWNT/ sodium silicate hybrid composites prepared from aqueous coating system (a) and EVOH coated nanofiller (b).

4. Conclusion

Current interest in nanocomposites has been generated and maintained because CNT-filled polymers exhibit unique combinations of properties not achievable with traditional composites. Some studies were carried out to investigate the properties and applicability of highly porous VOH group containing polymer/MWNT nanocomposites produced by simple saponification method. As has been shown in this study, the possible applications of highly porous MWNT nanocomposites range widely, from heating elements to polymeric filler. In addition, they can be easily processed by various techniques such as extruding, injection molding, laminating, film-casting, and printing. Since the nanocomposites prepared by this method have highly porous, good hydrophilicity, good mechanical strength and thermal properties, they can be used for various industrial applications.

Furthermore, MWNTs were subjected to electron-beam irradiation at various doses to determine the incidence of surface modification and, resultantly, deformation or destruction to the otherwise pristine graphitic structure. FTIR spectra obtained from electron-beam irradiated MWNT samples provide insight into the level of surface modification. Functional groups such like carboxyl and carbonyl groups on MWNT surface can interact with -OH group in polymer chains by hydrogen bonding and result in a better dispersion of MWNT

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in EVOH matrix. Such modified MWNT could be also functionalized to introduce covalent groups onto the nanotube surface, thus aiding in the uniform dispersion into polymer composite systems. Afterward we carry out extensive studies to investigate the properties and applicability for VOH group containing polymer coated and reacted nanotube prepared by simple saponification method.

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6. References

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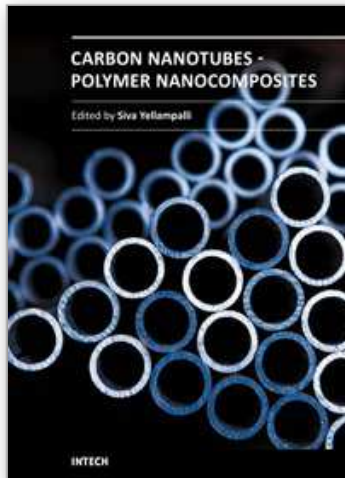
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Polymer nanocomposites are a class of material with a great deal of promise for potential applications in various industries ranging from construction to aerospace. The main difference between polymeric nanocomposites and conventional composites is the filler that is being used for reinforcement. In the nanocomposites the reinforcement is on the order of nanometer that leads to a very different final macroscopic property. Due to this unique feature polymeric nanocomposites have been studied exclusively in the last decade using various nanofillers such as minerals, sheets or fibers. This books focuses on the preparation and property analysis of polymer nanocomposites with CNTs (fibers) as nano fillers. The book has been divided into three sections. The first section deals with fabrication and property analysis of new carbon nanotube structures. The second section deals with preparation and characterization of polymer composites with CNTs followed by the various applications of polymers with CNTs in the third section.

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