Hydrophilic Encapsulation of Multi-Walled Carbon Nanotubes using Admicellar Polymerization

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ABSTRACT

Admicellar polymerization (AP), a surface analogue of emulsion polymerization was used to obtain a thin layer of hydrophilic polymer coating on multi-walled carbon nanotubes (MWCNTs). The hydrophilic nature can facilitate integration of carbon nanotubes into a variety of composite materials. To develop hydrophilic polymer by AP, acrylate monomers were copolymerized using sodium dodecyl sulfate as a surfactant. Development of a system for AP involves measurement of surfactant adsorption and adsolubilization or partitioning of monomer into adsorbed structures (reverse hemimicelles). A modified two-site adsolubilization model was used to calculate the size of surfactant aggregates over the surface of MWCNTs and a binary adsolubilization model was employed to predict number of monomers adsolubilized from single component experiments. Adsolubilized monomers were polymerized to form a polymer nanocomposite, which was then hydrolyzed to obtain a hydrophilic nanocomposite. SEM, Energy Dispersive Spectroscopy (EDS), Thermo Gravimetric Analysis (TGA) and FT-IR confirmed the formation of polymer on multi-walled carbon nanotubes (MWCNTs). Modified MWCNTs readily dispersed in aqueous media and were stable after 3 days.

Keywords

Adsorption isotherm; adsolubilization; polymer encapsulation; hydrophilic; multi-walled carbon nanotubes; co-polymer; nanocomposites; thin films.

1. INTRODUCTION

Carbon nanotubes (CNTs) are ideal reinforcing fibers for composites because of their high aspect ratio, high mechanical strength, and high electrical and thermal conductivity. Unfortunately, bundling due to intertube van der Waals and solvophobic interactions impairs many applications. Mixing of nanotubes with most common solvents or polymers results in formation of clumps, bundles and ropes. Dispersion of nanotubes in liquid media for separation of bundles generally requires surfactant or chemical functionalization of nanotubes, expanding applications of nanotubes to numerous fields. A number of groups have shown that imparting enhanced electrical, mechanical and thermal properties [1-8] to polymer composites with carbon nanotubes can be achieved by chemical modification or polymer encapsulation.

Nanocomposites can be expressed in two different forms, nanoparticles incorporated into a continuous bulk polymer matrix and discrete nanoparticles encapsulated in a thin film of polymer. Methods have been developed for each. Polymerization techniques like in situ polymerization[9], miniemulsion polymerization[10] and others [11, 12] are used to prepare nanocomposites that incorporate nanoparticles in polymer matrix. Discrete nanoparticles can be coated with a thin film using polymerization methods such as free radical polymerization[13, 14] and soap free emulsion polymerization[15]. Others have employed various techniques to apply polymer coatings like poly(methyl methacrylate)[16] and polyaniline[17] on CNT surfaces. Redispersion/solubilization of discrete nanocomposites often requires external means like sonication to dissolve them in aqueous media, since the polymers are hydrophobic. To increase the solubility of nanotubes in water, a hydrophilic polymer (e.g. polyacrylic acid[18] and polyacrylonitrile[19]) can be used. However, unfavorable bonding between a hydrophilic polymer and nanotubes might mean a poorly integrated unstable material. In particular, strongly hydrophilic polymer might dissolve away from nanotubes in aqueous media. Having a hydrophobic component can be expected to anchor the polymer or copolymer to MWCNTs. As one approach, copolymerization of a

hydrophilic monomer and a hydrophobic monomer on the surface of nanotubes might facilitate to redispersion/solubilization of modified MWCNTs in aqueous media without any external means.

In recent years, new routes of encapsulation of carbon nanotubes with a thin film of copolymer coating have appeared to enable new applications. Nanocomposites readily dispersible in water can be employed for bioelectrochemical reactions[20], radiation therapies[21] and drug delivery methods[22]. Mu et al[23] used surface-initiated atom transfer radical polymerization to obtain a double layer hybrid nanocomposite of MWCNTs with polystyrene as inner layer and polyacrylic acid doped polyacrylonitrile as outer layer. The hybrid nanocomposite is used as conductor-insulator-semiconductor sandwich-structured and is partially water-soluble. Wang et al[24] modified multi-walled carbon nanotubes by formation of block copolymer of poly(*tert*-butyl methacrylate) and polystyrene which was hydrolyzed to polymethacrylic acid (PMAA) and tested for dispersion stability in different solvents like water, ethanol, acetone and chloroform. Zou et al., prepared large compound vesicle functionalized MWCNTs using copolymer of poly(3-(trimethoxysilyl)-propyl methacrylate) and polyethylene glycol[25]. With polyethylene glycol being hydrophilic, biocompatible and nontoxic, the large-compound vesicle functionalized MWCNTs were water-soluble with potential use in drug delivery methods. A concern is that polymerization methods used to prepare copolymer of nanocomposites can degrade the electronic structure of nanotubes as the treatments often involve acids. Damage to the surface of carbon nanotubes surface can be mitigated by surfactant-assisted polymerization methods[13, 16, 19]. Association of monomer and nanotubes can be achieved on CNT surface without disturbing the π system while dispersion stability is high for nanocomposites prepared using surfactants. For example Xia et al. prepared nanocomposite of poly(methyl methacrylate-co-*n*-butyl acrylate) to disperse carbon nanotubes in latex using a surfactant assisted polymerization method[26] and Kim et al. developed redispersible SWCNTs in organic solvents using polymerizable surfactant by free radical polymerization[14] where the nanotube surfaces were not harmed.

In this paper we examine the application of an emulsion polymerization analogue, admicellar polymerization, to encapsulate multi walled carbon nanotubes (MWCNTs). The monomers butyl acrylate and methyl methacrylate are employed in combination with the surfactant sodium dodecyl sulfate to form a copolymer on carbon nanotubes. The copolymer formed on MWCNTs was hydrolyzed with sodium hydroxide to form hydrophilic encapsulated MWCNTs. The process of developing a system for admicellar polymerization involves measurement of surfactant adsorption and the adsolubilization or partitioning of monomers into adsorbed structures (reverse hemimicelles for MWCNTs). In addition modified two-site adsolubilization[27, 28] and binary adsolubilization[29] models were used to predict aggregation number and partition coefficients between surfactants structures and the bulk solution.

Aggregate morphology around nanotubes is still in debate with the most probable configurations proposed in literature being cylindrical micelles, hemispherical micelles, and a random layer[30]. Based on observations and literature, we assumed that, above a low threshold, the aggregate morphology around MWCNTs consists of a sleeve around nanotube surface. This structure allowed adaptation of the two-site adsolubilization model to estimate aggregation numbers. As initially conceived, the two-site adsolubilization model was based on disc shaped admicelles formed on hydrophilic substrates much larger in scale than CNTs. Our modification involves cylindrical shell around the surface of MWCNTs with a reverse hemimicellar configuration (Figure 1). The fundamental hypothesis for the model remains the same, that there are two sites at which monomers can be adsolubilized, one within the palisade layer and the other at the perimeter of aggregates. For the model, molecular parameters of surfactant and monomers (e.g., cross sectional areas of monomer headgroup (A_A)), were obtained from literature (details in Electronic Supplementary Material)[31]. From measurements of adsorption and adsolubilization, the aggregation number can be estimated using Equation 1.

$$N_{avg} = \frac{2\pi(l^2 + 2lR_n)}{A_A} \left(\frac{\Gamma_a}{\Gamma_s} - \left(\frac{K_b C_a}{1 - (K_b C_a)} \right) \right)^{-1} \quad (1)$$

Where N_{avg} is average aggregation number, R_n is radius of nanotube, l is the length of tail of surfactant molecule, A_A is cross-sectional area per monomer molecule, Γ_a is total amount of adsolubilized monomer, Γ_s is amount of surfactant adsorbed on MWCNTs, K_b is partition coefficient of monomer between hemimicellar and bulk phase, C_a is equilibrium concentration of monomer in supernatant.

Barton et al., developed a binary adsolubilization model to predict the amount of adsolubilized species from single component experiments[29]. That work was based on the partitioning of aliphatic alcohols into SDS aggregates over alumina. We extended the application of this model to investigate a reverse hemimicellar system formed on nanotube surface. In this approach one needs to specify the adsorbed amount of surfactant, which corresponds to specifying the extent of second phase or number of reverse hemimicelles. The partition coefficients can be determined from single component experimental data as it becomes constant at higher surfactant concentration. From Equation 2, we can predict number of moles of the two monomers adsolubilized in SDS reverse hemimicelles.

$$N_{tot} = \frac{VC_{1,0}N_{tot}K_1}{(K_1N_{tot}) + (VM_{sol})} + \frac{VC_{2,0}N_{tot}K_2}{(K_2N_{tot}) + (VM_{sol})} + \left((SDS)_0 - (SDS)_{eq} \right) V \quad (2)$$

Where N_{tot} is total number of moles in the reverse hemimicelles, N_1 and N_2 are moles of adsolubilized monomers, $C_{1,0}$ and $C_{2,0}$ are initial concentration of monomers, M_{sol} is molarity of water, K_1 and K_2 are partition coefficients of adsolubilized monomers and V is volume of aqueous phase.

2. EXPERIMENTAL

2.1 Materials

All chemicals were used as received. SouthWest Nano Technologies Inc. provided the multi-walled carbon nanotubes (MWCNTs) with a BET surface area of 295 m²/g. Sodium dodecyl sulfate (SDS) surfactant was purchased from Alfa Aesar USA while the monomers butyl acrylate (BA) and methyl methacrylate (MMA) were acquired from Sigma Aldrich USA. Initiator azobisisobutyronitrile (AIBN) was claimed from Fisher Scientific USA. Sodium hydroxide was obtained from EM Science USA.

2.2 Adsorption and Adsolubilization Analysis

MWCNTs (3 mg) were placed in 20 ml vials with SDS solutions at pH 7 of increasing concentrations from 0.01 mM to 100 mM. Samples were sonicated using sonic-dismembrator (Fischer Scientific F550) at 25% power setting for 10 min. Monomers with a total set concentration of 5 mM were added to vials. The samples were sealed with aluminum foil and capped with teflon-lined septa held in place with polypropylene caps without any headspace left in vials. Vials were placed in a shaker bath at room temperature for 14 hrs in order for adsorption and adsolubilization to occur. Amicon Ultra-0.5 centrifugal filter devices were used to separate supernatant surfactant solution from the MWCNTs using centrifuge at 10000 rpm for 30 min. A small aliquot from centrifuged vials was filtered with 0.45µm size filters for analysis by HPLC. Adsorption and adsolubilization measurements were determined from concentration changes by using a C18 surfactant column (RESTEK) (dimensions of 250mm x 4.6mm) with an evaporative light scattering detector for surfactant SDS and a UV-Vis detector for monomers BA (242nm) and MMA (231nm). Mobile phases used for analysis were methanol and water in ratios of 85:15 for SDS while monomers BA and MMA were assayed with similar mobile phase ratio. Calibration curves were obtained for surfactant and monomers followed by measurements to obtain adsorption isotherms and adsolubilization results.

2.3 Polymer Encapsulation

MWCNTs (10 mg) were placed in vials along with sodium dodecyl sulfate (6mM) solution. Samples were sonicated using an ultrasonic sonic dismembrator at room temperature for 10 min. Combination of monomers with a total concentration of 5mM were added to vials and placed in a shaker bath at 30°C for equilibration for 14 hrs for adsorption and adsolubilization to take place. Initiator concentration with a ratio of 1:2 with monomers was added to vials and polymerization reaction was carried out for 14 hrs at 80°C at 80 rpm in shaker bath. Samples were removed from shaker bath and vacuum dried at 80°C overnight. The samples were washed with methanol to remove trace amount of surfactant. To remove unreacted monomer and labile surfactant, samples were Soxhlet extracted with acetone for 48 hrs.

2.4 Hydrolysis

The dried samples after Soxhlet extraction were dissolved in 20 ml methanol and 1 ml of sodium hydroxide (5mM) dissolved in methanol was added to vials. Samples were placed in shaker bath at 100°C for 4 hrs for hydrolysis[32, 33]. Samples were washed with methanol and dried in vacuum for 12 hrs.

2.5 Characterization

2.5.1 Scanning Electron Microscopy (SEM)

The encapsulated nanotubes were examined by SEM using a Zeiss NEON high resolution SEM with a beam voltage of 5 keV. Samples for SEM were sputter coated with a thin layer of iridium.

2.5.2 Energy Dispersive Spectroscopy (EDS)

Energy dispersive spectroscopy (EDS) of encapsulated nanotubes before and after hydrolysis was carried out using INCA Energy 250 Energy Dispersive X-ray SEM microanalysis system with

analytical drift detector at beam energy of 5 keV. Elemental analyses provided an indication of carbon, oxygen, sodium and sulfur content on the surface of MWCNTs.

2.5.3 Thermo Gravimetric Analysis (TGA)

Thermo gravimetric analysis was performed using a NETZSCH STA 449F1 TG instrument. TGA studies were carried out as 10 mg samples in alumina crucibles. The flow rate of argon was 30 ml min⁻¹ with a protective inert gas argon flow rate of 20 ml min⁻¹. Temperature was increased from ambient temperature to 900 °C at a heating rate of 10°C min⁻¹.

2.5.4 Fourier Transform Infra-red Spectroscopy (FTIR)

Samples were weighed and mixed with KBr in mortar and pestle. Specac's Atlas series manual hydraulic press was used to prepare KBr pellets for FTIR analysis. FTIR spectra of samples were recorded by the KBr pellet testing techniques using Bruker Tensor 27 FTIR spectrophotometer in the wavenumber range from 4000 to 400 cm⁻¹ for 128 scans with a resolution of 4 cm⁻¹.

3. RESULTS AND DISCUSSION

3.1 Adsorption Isotherms

Adsorption isotherms of SDS alone and in presence of monomers (BA and MMA) are plotted in Figure 2. The adsorption isotherm obtained for MWCNTs is comparable to adsorption isotherms obtained by Mattaredona et al[34] on single wall carbon nanotubes (SWCNTs). As concentration of surfactant increases, adsorption increases and plateaus at or near CMC because available sites for adsorption on the nanotube surface decrease as the supernatant concentration increases. Adsorption of SDS on MWCNTs enhances the stabilization of nanotubes in water, as it diminishes the hydrophobic interactions between them. SDS produces an efficient surface coating that induces electrostatic or steric repulsions that counterbalances the van der Waals forces between MWCNTs.

As the supernatant concentration of SDS increases, presence of monomer BA has negligible effect on the adsorption isotherm. At intermediate concentrations of surfactant however MMA does seem to have an effect, as there is an increase in SDS adsorption. MMA, being poorly soluble in aqueous media, might have caused increased adsorption of SDS on MWCNTs surface. Monomer solubility influences the behavior in the system as it does in micellization, playing an important role in either increasing or decreasing the adsorption amounts of surfactants. SDS exhibits a peak adsorption of 2 g/g of nanotube alone and 3 g/g of nanotube in presence of BA and MMA monomer at around 10 mM supernatant concentration. Compared to adsorption of SDS on other surfaces like hydrotalcite[35], silica[36, 37] and alumina[38, 39], peak adsorption of SDS is higher on MWCNTs with and without presence of monomers. On the other hand peak adsorption on MWCNTs is less compared to single wall carbon nanotubes (SWCNTs) as the available surface for adsorption is higher for SWCNTs. The plateau in adsorption of SDS on the nanotubes occurs around 10 mM, near the critical micelle concentration (CMC). The presence of monomers has negligible effect on the CMC, but amount of SDS adsorbed on MWCNTs at CMC has increased.

3.2 Adsolubilization of Monomers

For adsolubilization of monomers (BA, MMA) on MWCNT surface, presence of surfactant is important. In absence of surfactant, monomer BA and MMA adsorption was negligible. Observations confirm that amount of monomer adsolubilized depends on the extent of adsorption of surfactant. The ratio of monomer adsolubilized to surfactant adsorbed decreases with increasing supernatant concentration of surfactant before beginning to level off at or near the CMC (Figure 3). This reflects a higher proportion of perimeter sites available for many small reverse hemimicelles at low coverage while core sites dominate as coverage approaches saturation. Findings attained by Yeskie et al[40] on alcohols have similar trends, the ratio of monomer decreases with increasing surfactant concentration which reflects the transition from

perimeter sites to palisade sites. In regions of high surface coverage, the ratio of monomer to surfactant decreases due to a balance between a loss of peripheral sites at edge of the surfactant aggregate and available space for monomer adsolubilization within the core of reverse hemimicelle. Determination of relative amounts of surfactant and monomer at the substrate surface for different system compositions helps to enhance understanding of the nature of reverse hemimicelle with adsolubilization and provides evidence for the two-site conceptualization.

3.3 Modified Two-site Adsolubilization Model

Patchwise adsorption of surfactant aggregates gives rise of the two-site adsolubilization model with species concentrating within the aggregate structure and at the periphery. The change in substrate to nanotubes necessitates a revision to the model. With an assumption that SDS on MWCNTs forms a reverse hemimicelle structure, a sleeve around the surface of nanotubes replaces the bilayer disc over alumina[27]. Two sites are formed on the surface, one in the palisade layer or core layer along the full length of the cylindrical shell (Figure 1) and the other at its two ends. Unlike the disc structure, peripheral sites do not increase with the size of aggregates, only with the number of aggregates. From Figure 4, as the density of surfactant increases, the aggregation number calculated from the model followed a near linear increasing trend on a log-log plot. Analysis with the modified two-site adsolubilization model yielded aggregation numbers ranging from order 10^3 to 10^5 . These values were similar to Lee et al[27]. For the nanotubes, aggregation numbers of adsorbed surfactants depend on substrate morphology as well as nature of the interaction of the adsolubilize. As the surfactant molecular density increases at solid/liquid interface, the sites available in the core region increase and Γ_c dominates.

3.4 Binary Adsolubilization Model

The binary adsolubilization model enables prediction of the number of monomer molecules at the solid/liquid interface in a multi component system from single component data. Barton et al.,

used the binary adsolubilization model to investigate separation of n-heptanol and 2-methyl-2-hexanol with sodium dodecyl sulfate surfactant admicelles[29]. It is necessary to specify the extent of adsorbed phase or number of hemimicelles, which is similar to predetermining the relative volume in a liquid-liquid extraction. We examined the suitability of the binary adsolubilization model to predict the number of monomer molecules adsolubilized in our reverse hemimicelle system. Table I (a, b, c) shows the results predicted versus observed for number of moles of monomer of BA and MMA with different ratios of monomers from 25:75, 50:50 and 75:25 with increasing surfactant concentration. Similar trends were found with predicted values being higher than observed at low surfactant coverage while being closer at higher levels of coverage. This makes sense since parameters used in the model are derived from the plateau region of the single component isotherms[29]. The deviation in predicted versus observed values at the low end of the isotherm is due to variation of partition coefficient and different reverse hemimicelle structures. At higher surfactant concentrations, predicted versus observed data looks similar because of formation of reverse hemimicelles on the surface of nanotube and stable monomer adsolubilization occurs in the core sites of reverse hemimicelles.

3.5 Polymer Encapsulation

SEM images obtained for pristine MWCNTs and for PBA-MWCNTs, PMMA-MWCNTs and PBA/PMMA-MWCNTs are shown in Figure 5. The average diameters of entangled nanotubes were measured using ImageJ image processing program. Polymer encapsulation by admicellar polymerization increases the diameter of MWCNTs (Table II) compared to diameter of pristine MWCNTs. The diameters (Table II) of PBA-MWCNTs, PMMA-MWCNTs and PBA/PMMA-MWCNTs were similar (13–15 nm) which confirms formation of polymer layer around 9 nm carbon nanotubes in all the samples. Thus the thickness of polymer around MWCNTs formed is about 5 nm. Compared to diameters in the range of 30-80 nm reported in previous works on

encapsulated MWCNTs, we achieved thin film encapsulation using admicellar polymerization on MWCNTs[16, 26].

To analyze the elemental composition, energy dispersive spectroscopy (EDS) was carried out on encapsulated MWCNTs before and after hydrolysis (Table III). Compared to pristine MWCNTs, carbon content is reduced and oxygen content increased in encapsulated samples. The change confirms formation of polymer as the polymer composition consists of mainly carbon and oxygen. The carbon content observed is higher than expected for polymers. When testing, high-energy x-ray beams can cause surface melting of polymer and expose the nanotubes, thus higher percentages of carbon are observed in all encapsulated samples. After hydrolysis of encapsulated MWCNTs with sodium hydroxide, oxygen and sodium content increased and carbon content decreased in PBA-MWCNTs and PBA/PMMA-MWCNTs as expected. The sulfur content was attributed to residual surfactant SDS, trace amounts present in all coated samples even after washing and using Soxhlet extraction.

FTIR spectra of PBA-MWCNTs, PMMA-MWCNTs and PBA/PMMA-MWCNTs are shown in Figure 6. Characteristic peaks of PBA and PMMA can be found in the respective samples. The C=O characteristic peak in carbonyl group at 1733 cm^{-1} is clear in all the samples as well as peaks at 2923 cm^{-1} and 2854 cm^{-1} corresponding to stretch mode of C-H bond vibration. The bending vibration of $-\text{CH}_2$ or $-\text{CH}_3$ groups at 1454 cm^{-1} and 1390 cm^{-1} are seen in all samples. Peaks between $1000\text{-}1200\text{ cm}^{-1}$ can be attributed to stretching vibration of C-O group of polymer. In samples after hydrolysis, the significant peak for PBA-MWCNTs and PBA/PMMA-MWCNTs between $1350\text{-}1500\text{ cm}^{-1}$ which corresponds to bending vibration of $-\text{CH}_2$ and C-O bonds for carboxylic acids and salts of acetate, which are formed during hydrolysis of acrylate polymers[41].

From SEM micrographs, FTIR and EDS analysis, polymer formation on MWCNTs was confirmed. Thermo gravimetric analysis was implemented on samples to obtain the percentage of polymer content in polymer encapsulated MWCNTs. Figure 7 shows TGA curves of pristine MWCNTs, PBA-MWCNTs, PMMA-MWCNTs and PBA/PMMA-MWCNTs before and after hydrolysis. The pristine carbon nanotubes have high thermal stability and almost negligible weight loss after heating to 900°C. In case of samples before hydrolysis, the weight loss observed due to polymer decomposition before 400°C signifies a 25-30% polymer content in the samples. Two stages of decomposition mechanism were observed in samples before hydrolysis. At around 650°C, there is an additional loss of around 25-30% indicating decomposition of higher molecular weight fragments formed during the first stage decomposition and leaving nanotubes thereafter. After hydrolysis, hydrolyzed PBA-MWCNTs and PMMA-MWCNTs have weight loss of approximately 20% compared to 25% for PBA/PMMA-MWCNTs. A difference of about 5-10% higher weight loss was found in samples after hydrolysis. The thermal stability of polymer formed after hydrolysis is higher than the thermal stability of polymer before hydrolysis. The butyl moiety has higher mass than is present after hydrolysis, contributing to the larger weight loss. Formation of sodium salt of poly acrylic acid after hydrolysis affects the decomposition rate of polymer. Large ester groups on poly butyl acrylate polymers tend to form poly acrylic acid and corresponding olefins by a molecular ester decomposition mechanism[42] under thermal analysis but degradation of poly acrylic acid under thermal analysis occurs using by decarboxylation mechanism[43, 44]. PBA-MWCNTs had higher polymer content than PMMA-MWCNTs because of relatively low hydrophobic properties of MMA monomer compared to BA monomer[16].

From above analytical techniques, polymer formation before and after hydrolysis was confirmed. To analyze the dispersion stability of the polymer formed on MWCNTs after hydrolysis, MWCNTs were dispersed in aqueous media and left aside for 3 days. In Figure 8, hydrolyzed PBA-MWCNTs and hydrolyzed PBA/PMMA - MWCNTs were stable even after 3 days but

PMMA-MWCNTs formed aggregates and settled at the bottom of the vial. Hydrolysis of PBA to form salts of poly acrylic acid increases the dispersion of nanotubes without any external means like sonication. Thus the formation of hydrophilic polymer after hydrolysis influences the dispersion stability of MWCNTs in aqueous media.

4. CONCLUSION

Admicellar polymerization was successfully employed to form copolymer of hydrophilic and hydrophobic characteristics around the surface of MWCNTs. Adsorption and adsolubilization measurements were obtained for SDS surfactant and acrylate monomers. Presence of monomer has increased the peak adsorption of SDS on MWCNTs around CMC of surfactant. The ratio of monomer adsolubilized versus surfactant decreases with increasing surfactant concentration before beginning to level off at or near CMC of surfactant. For nanotubes, aggregation number of surfactants depends on the morphology of substrate. Aggregation numbers were estimated using a modified two-site adsolubilization model and sleeves as the structure formed on the MWCNTs surface. We examined the suitability of binary adsolubilization to predict the number of moles of monomer solid/liquid interface. Surface analytical techniques confirm the presence of copolymer of PBA and PMMA on the surface of nanotubes. Film thickness of around 5 nm was formed around surface of MWCNTs. The modified MWCNTs easily dispersed in aqueous media and remained stable even after 3 days.

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REFERENCES

1. C.S. Velasco, H.A.L. Martinez, F.T. Fisher, R. Ruoff, V.M. Castano, Improvement of thermal and mechanical properties of carbon nanotube composites through chemical functionalization, *Chem. Mater.* 15 (2003) 4470-4475.
2. J. Wang, F. Zhengping, G. Aijuan, X. Lihua, L. Fu, Effect of amino-functionalization of multi-walled carbon nanotubes on the dispersion with epoxy resin matrix, *J. Appl. Polym. Sci.* 100 (2006) 97-104.
3. Y.T. Sung, M.S. Han, K.H. Song, J.W. Jung, H.S. Lee, C.K. Kum, J. Joo, W.N. Kim, Rheological and electrical properties of polycarbonate/multi-walled carbon nanotube composites, *Polymer*. 47 (2006), 4434-4439.
4. Q. Jingjing, C. Zhang, B. Wang, R. liang, Carbon nanotube integrated multifunctional multiscale composites, *Nanotechnology*. 18 (2007), 275708.
5. W. Zou, D. Zhong-jie, L. Yan-xin, Y. Xiaoping, L. Hang-quan, C. Zhang, Functionalization of MWNTs using polyacryloyl chloride and the properties of CNT-epoxy matrix nanocomposites, *Compos. Sci. Technol.* 68 (2008), 3259-3264.
6. H. Meng, G.X. Sui, P.F. Fang, R. Yang, Effects of acid- and diamine-modified MWNTs on the mechanical properties and crystallization behavior of polyamide 6, *Polymer*. 49 (2008) 610-620.

7. D. Wu, L. Wu, M. Zhang, Y. Zhao, Viscoelasticity and thermal stability of polylactide composites with various functionalized carbon nanotubes, *Polym. Degrad. Stabil.* 93 (2008) 1577-1584.
8. P.A. Song, L. Xu, Z. Guo, Y. Zhang, Z. Fang, Flame-retardant-wrapped carbon nanotubes for simultaneously improving the flame retardancy and mechanical properties of polypropylene, *J. Mater. Chem.* 18 (2008) 5083-5091.
9. S.J. Park, M.S. Cho, S.T. Lim, H.J. Choi, M.S. Jhon, Synthesis and dispersion characteristics of multi-walled carbon nanotube composites with poly(methyl methacrylate) prepared by in-situ bulk polymerization, *Macromol. Rapid. Comm.* 24 (2003) 1070-1073.
10. H.J. Barraza, F. Pompeo, E.A. O'Rear, D.E. Resasco, SWNT-filled thermoplastic and elastomeric composites prepared by miniemulsion polymerization, *Nano Letters.* 2 (2002) 797-802.
11. D. Blond, V. Barron, M. Ruether, K.P. Ryan, V. Nicolosi, W.J. Blau, J.N. Coleman, Enhancement of modulus, strength, and toughness in poly(methyl methacrylate)-based composites by the incorporation of poly(methyl methacrylate)-functionalized nanotubes, *Adv. Funct. Mater.* 16 (2006) 1608-1614.
12. O. Regev, P.N.B. Elkati, J. Loos, C.E. Koning, Preparation of conductive nanotube-polymer composites using latex technology, *Adv. Mater.* 16 (2004) 248-251.
13. G. Guo, D. Yang, C. Wang, S. Yang, "Fishing" polymer brushes on single-walled carbon nanotubes by in-situ free radical polymerization in a poor solvent, *Macromolecules.* 39 (2006) 9035-9040.

14. T.H. Kim, C. Doe, S.R. Kline, S.M. Choi, Organic solvent-redispersible isolated single wall carbon nanotubes coated by in-situ polymerized surfactant monolayer, *Macromolecules*. 41 (2008) 3261-3266.
15. Z. Cheng, Q. Pan, G.L. Rempel, Modification of multiwall carbon nanotubes via soap-free emulsion polymerization of acrylonitrile, *J. Polym. Sci. Pol. Chem.* 48 (2010) 2057-2062.
16. H. Xia, Q. Wang, G. Qiu, Polymer-encapsulated carbon nanotubes prepared through ultrasonically initiated in situ emulsion polymerization, *Chem. Mater.* 15 (2003) 3879-3886.
17. F. Huang, E. Vanhaecke, D. Chen, In situ polymerization and characterizations of polyaniline on MWCNT powders and aligned MWCNT films, *Catal. Today*. 150 (2010) 71-76.
18. W. Zhong, J. N. Zeuna, J. P. Claverie, A versatile encapsulation method of noncovalently modified carbon nanotubes by RAFT polymerization, *J. Polym. Sci. Pol. Chem.* 50 (2012) 4403-4407.
19. C. Poochai, T. Pongprayoon, Enhancing dispersion of carbon nanotube in polyacrylonitrile matrix using admicellar polymerization, *Colloids. Surface. A*. 456 (2014) 67-74.
20. V. Urbanová, L. Allai, W. Ghach, V. Maname, M. Etienne, M. Dossot, A. Walcarius, Functionalized carbon nanotubes for bioelectrochemical applications: Critical influence of the linker, *J. Electroanal. Chem.* 707 (2013) 129-133.
21. B.P. Jiang, L.F. Hu, X.C. Shen, S.C. Ji, Z. Shi, C.J. Liu, L. Zhang, H. Liang, One-Step Preparation of a Water-Soluble Carbon Nanohorn/Phthalocyanine Hybrid for Dual-

- Modality Photothermal and Photodynamic Therapy, ACS Appl. Mater. Interface. 6 (2014) 18008-18017.
22. T.L. Moore, S.W. Grimes, R.L. Lewis, F. Alexis, Multilayered polymer-coated carbon nanotubes to deliver dasatinib, Mol. Pharmaceutics. 11 (2013) 276-282.
 23. B. Mu, P. Liu, X. Yu, F. Pan, Z. Gao, X. Liu, Preparation and characterization of conductor–insulator–semiconductor sandwich-structured MWCNT/double-layer polymer hybrid nanocomposites, Synthetic. Met. 160 (2010) 2329-2335.
 24. G. Wang, J. Yang, Y. Wang, Y. Liu, Self-assembly behavior of carbon nanotubes modified by amphiphilic block copolymer, Colloid. Polym. Sci. 288 (2010), 1677-1685.
 25. P. Zou, G.Y. Shi, C.Y. Pan, Large-compound vesicle-encapsulated multiwalled carbon nanotubes: A unique route to nanotube composites, J. Polym. Sci. Pol. Chem. 47 (2009) 3669-3679.
 26. H. Xia, G. Qiu, Q. Wang, Polymer/carbon nanotube composite emulsion prepared through ultrasonically assisted in situ emulsion polymerization, J. Appl. Polym. Sci. 100 (2006) 3123-3130.
 27. C. Lee, M.A. Yeskie, J.H. Harwell, E.A. O'Rear, Two-site adsolubilization model of incorporation of alcohols into adsorbed surfactant aggregates, Langmuir. 6 (1990) 1758-1762.
 28. S. Hanumansetty, E.A. O'Rear, Two-Site adsolubilization model of incorporation of fluoromonomers into fluorosurfactants formed on cotton fabric, Langmuir. 30 (2014) 3665-3672.

29. J.W. Barton, T.P. Fitzgerald, C. Lee, E.A. O'Rear, J.H. Harwell, Admicellar chromatography: separation and concentration of isomers using two-dimensional solvents, *Separ. Sci. Technol.* 23 (1988) 637-660.
30. W.H. Duan, Q. Wang, F. Collins, Dispersion of carbon nanotubes with SDS surfactants: a study from a binding energy perspective, *Chem. Sci.* 2 (2011) 1407-1413.
31. M.J. Rosen, Micelle formation by surfactants, in: *Surfactants and Interfacial Phenomena*. John Wiley & Sons, Inc. 2004, pp.105-177.
32. A. Maeder, Salts of hydrolyzed polyacrylate esters and solutions thereof. U.S. Patent 2,897,172, July 28, 1959.
33. V. Theodorou, K. Skobridis, A.G. Tzakos, V. Ragoussis, A simple method for the alkaline hydrolysis of esters, *Tetrahedron. Lett.* 48 (2007) 8230-8233.
34. O. Matarredona, H. Rhoads, Z. Li, J.H. Harwell, L. Balzano, D.E. Resasco, Dispersion of single-walled carbon nanotubes in aqueous solutions of the anionic surfactant NaDDBS, *J. Phys. Chem. B.* 107 (2003) 13357-13367.
35. K. Esumi, S. Yamamoto, Adsorption of sodium dodecyl sulfate on hydrotalcite and adsolubilization of 2-naphthol, *Colloids. Surfaces. A.* 137 (1998) 385-388.
36. A. Berthod, I. Girard, C. Gonnet, Micellar liquid chromatography, adsorption isotherms of two ionic surfactants on five stationary phases, *Anal. Chem.* 58 (1986) 1356-8.
37. M.M. Mohamed, Adsorption properties of ionic surfactants on molybdenum-modified silica gels, *Colloids. Surfaces. A.* 108 (1996) 39-48.
38. W. Wang, J. C. T. Kwak, Adsorption at the alumina–water interface from mixed surfactant solutions, *Colloids. Surfaces. A.* 156 (1999) 95-110.

39. K. Sakagami, T. Yoshimura, K. Esumi, Simultaneous adsorption of poly(1-vinylpyrrolidone-co-acrylic acid) and sodium dodecyl sulfate at alumina/water interface, *Langmuir*. 18 (2002) 6049-6053.
40. M.A. Yeskie, Various aspects of surfactant aggregates adsorbed on an oxide surface: The hemimicelle/admicelle transition, and the interaction of alcohols and alkanes. Chemical Bio and Materials Engineering Department, University of Oklahoma, Norman, OK, 1988.
41. M.H.S. Alavi, M. Habibi, R. Amrollahi, F. A. Taromi, A Study on Plasma Polymerization of Acrylic Acid Using APF Plasma Focus Device, *J. Fusion. Energ.* 30 (2011) 184-189.
42. Y.H. Hu, C.Y. Chen, C.C. Wang, Thermal degradation kinetics of poly(n-butyl acrylate) initiated by lactams and thiols, *Polym. Degrad. Stabil.* 84 (2004) 505-514.
43. I.C. McNeill, S.M.T. Sadeghi, Thermal stability and degradation mechanisms of poly(acrylic acid) and its salts: Part 1—Poly(acrylic acid), *Polym. Degrad. Stabil.* 29 (1990) 233-246.
44. S. Dubinsky, G.S. Grader, G.E. Shter, M.S. Silverstein, Thermal degradation of poly(acrylic acid) containing copper nitrate, *Polym. Degrad. Stabil.* 86 (2004) 171-178.

FIGURE CAPTIONS

Figure 1. Schematic view of modified two-site adsolubilization model (a) Sleeve model showing monomer at peripheral site (b) Cross-sectional view with monomer in the core (Γ_c is amount of monomer adsolubilized in palisade layer of hemimicelle, Γ_p is amount of monomer adsolubilized on perimeter of hemimicelle)

Figure 2. Adsorption isotherm of SDS without and with presence of monomers.

Figure 3. Ratio of monomer (BA and MMA) to surfactant (SDS)

Figure 4. Aggregation number calculated using modified two-site adsolubilization model.

Figure 5. SEM analysis of 1. Pristine MWCNTs, 2. PBA-MWCNTs, 3. PMMA-MWCNTs, 4. PBA/PMMA-MWCNTs.

Figure 6. FTIR analysis of encapsulated MWCNTs before and after hydrolysis.

Figure 7. TG analysis of pristine MWCNTs and encapsulated MWCNTs.

Figure 8. Encapsulated MWCNTs dispersed in water. Picture was taken after 3 days dispersion in water.

Table I (a). Comparison of predicted versus observed for total number of moles in reverse hemimicelle and moles of BA and MMA monomers (ratio 75:25)

BA: MMA - 75:25					
SDS+BA+MMA		BA		MMA	
N_{Total}		N₁		N₂	
Predicted	Observed	Predicted	Observed	Predicted	Observed
38.54	7.14	25.65	3.37	12.58	2.14
68.79	29.37	35.92	9.94	20.64	6.97
96.05	93.54	47.94	32.36	31.44	24.24
175.91	170.82	84.94	74.58	47.83	50.87
272.92	260.86	113.33	97.14	70.10	49.32
320.60	311.48	150.67	136.33	86.01	73.92

Table I (b). Comparison of predicted versus observed for total number of moles in reverse hemimicelle and moles of BA and MMA monomers (ratio 50:50)

BA: MMA - 50:50					
SDS+BA+MMA		BA		MMA	
N_{Total}		N₁		N₂	
Predicted	Observed	Predicted	Observed	Predicted	Observed
38.26	9.21	23.53	3.73	11.49	2.77
79.89	26.44	38.42	9.56	25.97	9.14
113.31	129.10	54.09	56.67	42.02	45.69
185.31	175.43	75.02	68.48	70.25	69.14
292.50	287.08	95.90	93.31	86.16	84.44
371.77	351.20	106.40	96.75	96.87	107.90

Table I (c). Comparison of predicted versus observed for total number of moles in reverse hemimicelle and moles of BA and MMA monomers (ratio 25: 75)

BA: MMA - 25:75					
SDS+BA+MMA		BA		MMA	
N_{Total}		N_1		N_2	
Predicted	Observed	Predicted	Observed	Predicted	Observed
39.02	9.09	8.75	1.86	24.31	3.72
67.42	31.42	19.48	4.97	37.59	8.94
88.23	83.69	27.09	19.29	45.33	37.43
154.05	149.38	45.91	39.43	75.45	71.42
220.86	213.81	66.16	62.19	92.52	87.13
353.34	338.15	88.78	85.22	140.47	136.97

Table II. Average diameter of pristine MWCNTs and encapsulated MWCNTs

Type	Diameter (nm)
MWCNTs	9.1
MWCNTs with PBA	13.3
MWCNTs with PMMA	14.5
MWCNTs with PBA/PMMA	14.6

Table III. EDS analysis of encapsulated MWCNTs before and after hydrolysis

Sample	Carbon	Oxygen	Sodium	Sulphur
	Before hydrolysis (wt.%)			
MWCNTs	97	1.5	0	0
PBA-MWCNTs	73.7	15.2	10.2	0.9
PMMA-MWCNTs	82.3	10.7	5.9	1.1
PBA/PMMA MWCNTs 75:25	78.4	12.3	7.4	0.4
After hydrolysis (wt.%)				
Hydrolyzed PBA-MWCNTs	66.6	18.1	17.2	0.9
Hydrolyzed PMMA-MWCNTs	80.6	11.8	6.5	1.1
Hydrolyzed PBA/PMMA MWCNTs 75:25	73.1	16.7	9.5	0.4

Figure 1a

Figure 1b

Figure(s)

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Figure 2

Figure 3

Figure 4

Figure(s)

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Figure 5.1

Figure(s)

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Figure 5.2

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Figure 5.3

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Figure 5.4

After Hydrolysis

Figure 6

Before Hydrolysis

Figure 6 cont

Figure 7

Figure(s)

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Figure 8