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S. Sahebian^a, S. Mojtaba Zebarjad^a, J. Vahdati-Khaki^a & A. Lazzeri^b

^a Department of Materials Science and Engineering, Engineering Faculty, Ferdowsi University of Mashhad, Mashhad, Iran

^b Department of Chemical Engineering, University of Pisa, Pisa, Italy

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On the Role of Stearic Acid on the Surface Properties of Carbon Nanotubes

S. SAHEBIAN,¹ S. MOJTABA ZEBARJAD,¹ J. VAHDATI-KHAKI,¹ and A. LAZZERI²

¹Department of Materials Science and Engineering, Engineering Faculty, Ferdowsi University of Mashhad, Mashhad, Iran

²Department of Chemical Engineering, University of Pisa, Pisa, Italy

In this article, modification of multiwalled carbon nanotubes (MWCNTs) with stearic acid (SA) was done using the wet chemical method. For this aim, MWCNTs were treated with high-concentrated nitric acid to create a functional group as a linkage between MWCNTs and SA. The modified MWCNTs with SA were examined by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), differential scanning calorimeter (DSC), and thermogravimetry analysis (TGA) instruments. The results of TGA and DSC indicate the deposition of about 4.3 wt% of SA on the surface of MWCNTs. This proves that the deposition of stearate with a medium diameter size of 20 nm on the surface of MWCNTs can be divided into physical and chemical adsorption. As well, the esterification occurs on the surface of functionalized MWCNTs and there is no SA unreacted on the surface of MWCNTs.

Keywords: Multiwall carbon nanotube, stearic acid, wet chemical treatment

Introduction

Uniform and stable dispersion of particles in media and composites is a very important matter for many industrial applications. This requirement is especially critical when submicron or nanometer sized particles are used in the final product and is related to surface chemistry that controls the dispersion of filler in matrix. The ability of surfactants to accumulate on surfaces or interfaces has been widely used to promote stable dispersions of solids in different media due to reduction of surface tension (Dai et al. 1996; Martel et al. 1998; Kong et al. 2001; Liu et al. 2002; Chen et al. 2005; Menzel et al. 2009). Carbon nanotubes (CNTs) with superior physical and chemistry properties are attracting a great deal of interest in many potential applications, such as nanoelectronics, composites, and electrochemical storage of energy (Dai et al. 1996; Martel et al. 1998; Kong et al. 2001; Liu et al. 2002; Menzel et al. 2009).

In order to produce nanocomposites with high performance, it is necessary to have good dispersion and stability of CNTs in the matrix. Since CNTs are chemically inert, having neither hydrophilicity nor lipophilicity, the use of CNTs as reinforcing elements will result in poor dispersion capability and weak interfacial interactions. Also, bundles (or ropes) with a van der Waals binding energy of

approximately 500 eV per micrometer of tube–tube contact can be formed as highly polarizable nanotubes. Therefore, activating and modifying their surface is an essential pre-treatment (Chen et al. 2005). Chemical modification of CNTs not only improves their dispersity in solvents and composites, but also enhances their compatibility with the matrix.

CNTs can be dispersed in composite and media when coated with adsorbed surfactants. The nature of the surfactant, its concentration, and type of interaction are known to play critical roles in the dispersion behavior of CNTs (Datsyuk et al. 2002). There has been some research published related to surfactant as coating of CNT; for example, Liu et al. (2002) made new solubilized multiwalled carbon nanotubes derivatives by reacting the surface bonded carboxylic groups with dodecylamine. It has been reported that CNTs can be modified by monoamine terminated polyethylene oxide (PEO), but due to the hydrophilic nature of PEO, the modified CNTs were only kinetically stable when dispersed at the air–water interface (Pompeo and Resasco 2002). Octadecyl-amide functionalized MWNT have been reported to exhibit good solubility in carbon disulfide (CS₂) and toluene (Qin et al. 2003), as well as have improved dispersion in polypropylene (PP) matrix (Vaisman and Wagner 2006).

Chen et al. (2005) showed that esterification in water media was formed in the oxidized MWNTs and stearic acid (SA). In this method, H₂SO₄ as catalyst was used in water/MWCNTs media to activate the functional group on the surface of MWCNT. Then these active groups on the surface of MWCNTs react with SA as the esterification reaction.

Address correspondence to: S. Mojtaba Zebarjad, Department of Materials Science and Engineering, Engineering Faculty, Ferdowsi University of Mashhad, Azadi Square, Mashhad, P.O. Box 91775-1111, Iran. E-mail: Zebarjad@um.ac.ir
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The SA linkages on MWCNTs led to an improvement in the dispersion of MWNTs and the tribological properties of MWNTs as a lubricant additive.

It has been known for long time that stearic acid acts as a surfactant in polymer composites, especially for polyethylene/particle composites. However, there is little in the literature showing the use of stearic acid in polymer/CNT composites. For this reason the authors tried to find good way for coating CNT with SA, for which afterward the modified reinforcement will be used in polyethylene composites and the results to be used elsewhere.

Experimental

Materials

MWNTs were obtained from Nanolin (China) with outer diameters in the range of 40 to 60 nm, length of 5–15 μm , and purity greater than 95%. SA with specific code of 410977, melting temperature of 69°C, and molecular weight of 284.47 was purchased from Carlo Erba (France).

Acid Treatment of MWNTs

An amount of 50 ml concentrated HNO_3 (68 wt%) was added to 0.1 g MWNTs. The mixture was sonicated in a water bath for 2 h at room temperature, then stirred at same temperature for 2 h. The mixture was filtered by using deionized water for several times until pH reached 6. The opened MWNTs were dried at 90°C overnight.

Surface Coating of FMWCNT by SA

The oxidized CNTs were mixed in acetone for 60 min by using an ultrasonic bath. Some SA powders were added to acetone and stirred under 80°C. The liquid media, including SA, was added to MWCNTs media and stirred under 80°C for 4 h. The reaction mixture was cooled to room temperature and extracted with chloroform. In order to remove residual SA, the resulting MWCNTs were further rinsed with hexane or cyclohexane. After filtering and washing with acetone, the samples were dried at 80°C under vacuum oven for overnight.

For simplicity, pure MWCNTs, functionalized MWCNTs, and functionalized MWCNT coated with SA were coded PCNT, FCNT, FSA-1, respectively.

Instruments

In order to perform microscopic evaluation of the samples, a TEM LEO 912 AB., TEM LEO 912 AB was selected in line resolution of 3Å and operated at 120 kV. The thermogravimetric analysis (TGA) was studied using a thermal analysis system (TGA50, Shimadzu, Japan) in N_2 atmosphere. Differential scanning calorimeter (DSC) measurements were done in air atmosphere using a TA Q200 instrument at a heating rate of 10°C/min. Fourier transform infrared spectroscopy measurement (FTIR) was performed on a magna-IR 560 E.S.P. FTIR spectrometer. x-ray

diffraction (XRD) pattern of samples were recorded with PC1800 diffractometer using $\text{Cu } k_\alpha$ radiation.

Results and Discussion

In order to investigate the morphology and formation of SA on the surface of MWCNTs, TEM images were taken from PCNT, FCNT, and FSA1. Figures 1a and 1b display the morphology of pure and functionalized MWCNTs. After acid treatment, the end caps of MWCNTs were almost opened and some defects were shown on the surface of MWCNTs.

Figure 2 indicates a uniform deposition of the SA particles on the surface of CNTs. The SA particles have a round shape and an average size of about 20 nm. Also, we see a selected area diffraction (SAED) pattern, calculated from the part of the SA particle contained in the frame, where the diffraction rings correspond to the SA particles on the surface of CNTs, which is consistent with XRD results.

The presence of SA in FSA-1 samples was proved by TEM, The main question to look at, however, is if this SA is related to free SA or reacted with CNTs. Therefore, FSA-1 samples, after and before washing with cyclohexane, were examined by DSC as seen in Figure 3. According to Figure 3, before washing by cyclohexane, there is sharp large peak related to melting of SA around 60°. It is concluded that there are a lot of free SA in the samples. However, after washing with cyclohexane, there is no significant peak around 60°C, which indicates unreacted SA in FSA-1 samples was eliminated. This result is compatible with the TEM data that implies the decoration of MWCNTs with SA, and proves that washing by cyclohexane can be the main step for covering with SA. For this reason, other evaluations on the FSA-1 sample were done after washing by cyclohexane.

XRD patterns of PCNT, FCNT, and FSA1 samples are shown in Figure 4, with the main peak at 26.1° and other peaks of 42.7°, 53.8°, and 77.6° that are related to graphite structure. As well, three peaks at 20.8, 21.68°, and 24.2° of SA are shown in the pattern, but since the other peaks of SA overlapped with the diffraction pattern of graphite, they are not completely clear. In summary, these three peaks of SA (at 20.8, 21.68°, and 24.2°) prove the presence of SA on the surface of FMCNT.

Figure 5 shows the esterification reaction mechanism of SA with hydroxyl group on the surface of FCNT in acetone media. As seen from Figure 5, in order to create linkage between SA and FCNT, the presence of hydroxyl and carboxyl groups on the surface of MWCNTs is necessary. So, before chemical treatment by SA, acid treatment of MWCNTs must occur. Again, as seen in Figure 5, these groups have a free electron site to react with a positive charge in SA groups.

Figure 6 shows the FTIR spectrum of PCNT, FCNT, SA, FCNT +SA, and FSA-1. The PCNT samples do not have special groups on the surface; there is only one hydroxyl group due to humidity in samples. Functionalized MWCNTs show many groups on the surface, such as

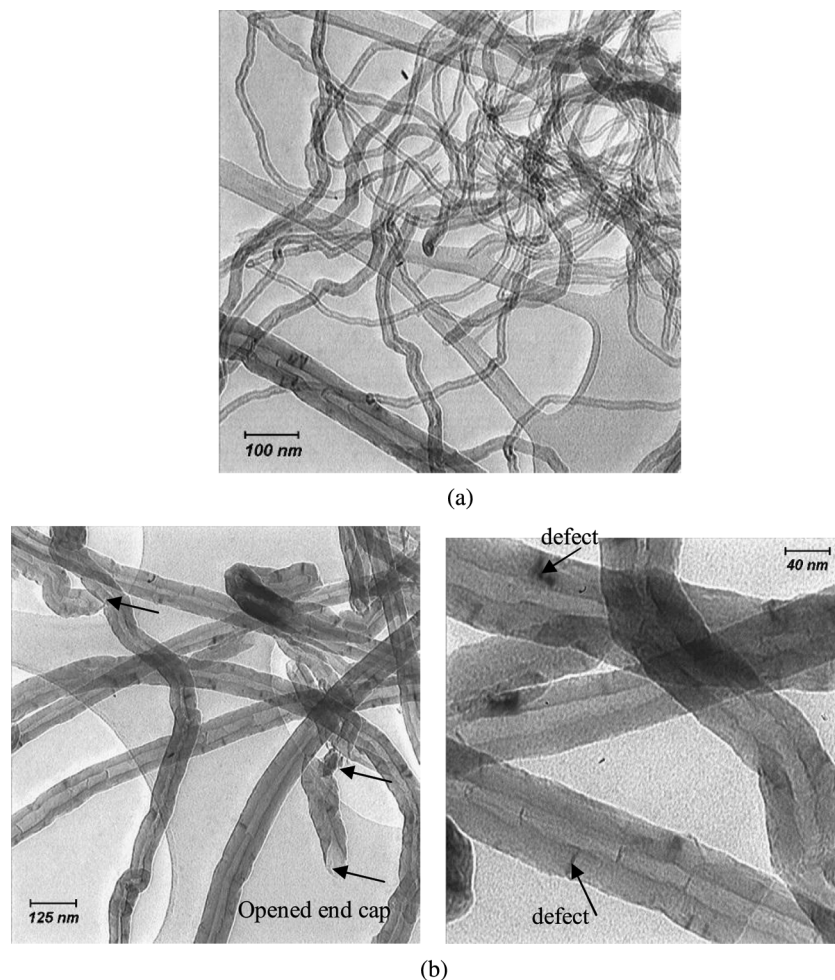


Fig. 1. TEM images of a) PCNT and b) FCNT.

carbonyl group at 1720 cm^{-1} , hydroxyl group in the region of $3600\text{--}3800\text{ cm}^{-1}$, and a small peak at around 2900 cm^{-1} that is related to CH_3 and CH_2 stretching mode. After SA treatment, the characteristic peaks of SA were observed at around 2940 , 2860 , 1360 , and 1040 cm^{-1} , respectively. The two new peaks at 2940 cm^{-1} and 2860 cm^{-1} are related to CH_3 and CH_2 stretching mode. Also, the new peak observed at about 1492 cm^{-1} should be attributed to COO^- , which was considered as a shift from COOH to COO^- , as shown in Figure 5. This confirms the effect of linkage between the OH on MWNTs and COOH on SA due to the esterification reaction. Furthermore, the strong peaks seen at about 1492 cm^{-1} may be attributed to the carboxyl groups of SA. The result showed that SA has a chemical reaction with the surface of MWNTs through the esterification reaction.

In order to calculate the weight percent of SA forming on the surface of FCNT, TGA is used. Figure 7 shows the weight loss and derivative weight loss of FCNT, SA, and FSA-1 samples versus temperature. Figure 8 is close up of this graph to completely clarify the degradation of FSA-1 and FCNT samples. Figure 8 shows the degradation of SA completely is done at single peak in a temperature range of 190°C to 280°C , unlike the FSA-1 samples, which have

two separated degradation peaks. The first degradation stage of the FSA-1 sample is related to degradation of SA linkage on the surface of CNT, and the second weight loss stage of the FSA-1 sample is connected to CNT degradation. As seen in Figure 7, the degradation starts at a higher and wider temperature range that is the evidence for chemical bond between SA and CNT and the decomposition of SA occurs around 200°C , unlike FSA-1. Also, according to weight loss data of the FSA-1 sample, about 4.3 wt% of SA is formed on the surface of CNTs.

Figure 8 demonstrates the variation of weight loss and derivative weight loss of the FCNT and FSA-1 samples versus temperature. The degradation of FCNT has two weight loss steps until the temperature reaches 1000°C . It seems as the temperature increases to 600°C , hydroxyl and carboxyl groups form on the surface of CNTs after acid treatment. The second stage starts at around 740°C , which is correlated to the degradation of CNTs. As explained earlier, the degradation of FSA-1 has two steps similar to the FCNT sample, although the first stage is related to SA degradation.

Another interesting result from the derivative thermogravimetry curve seen in Figure 7 is the separation of two peaks in the range of 200°C to 500°C for the FCNT sample. The

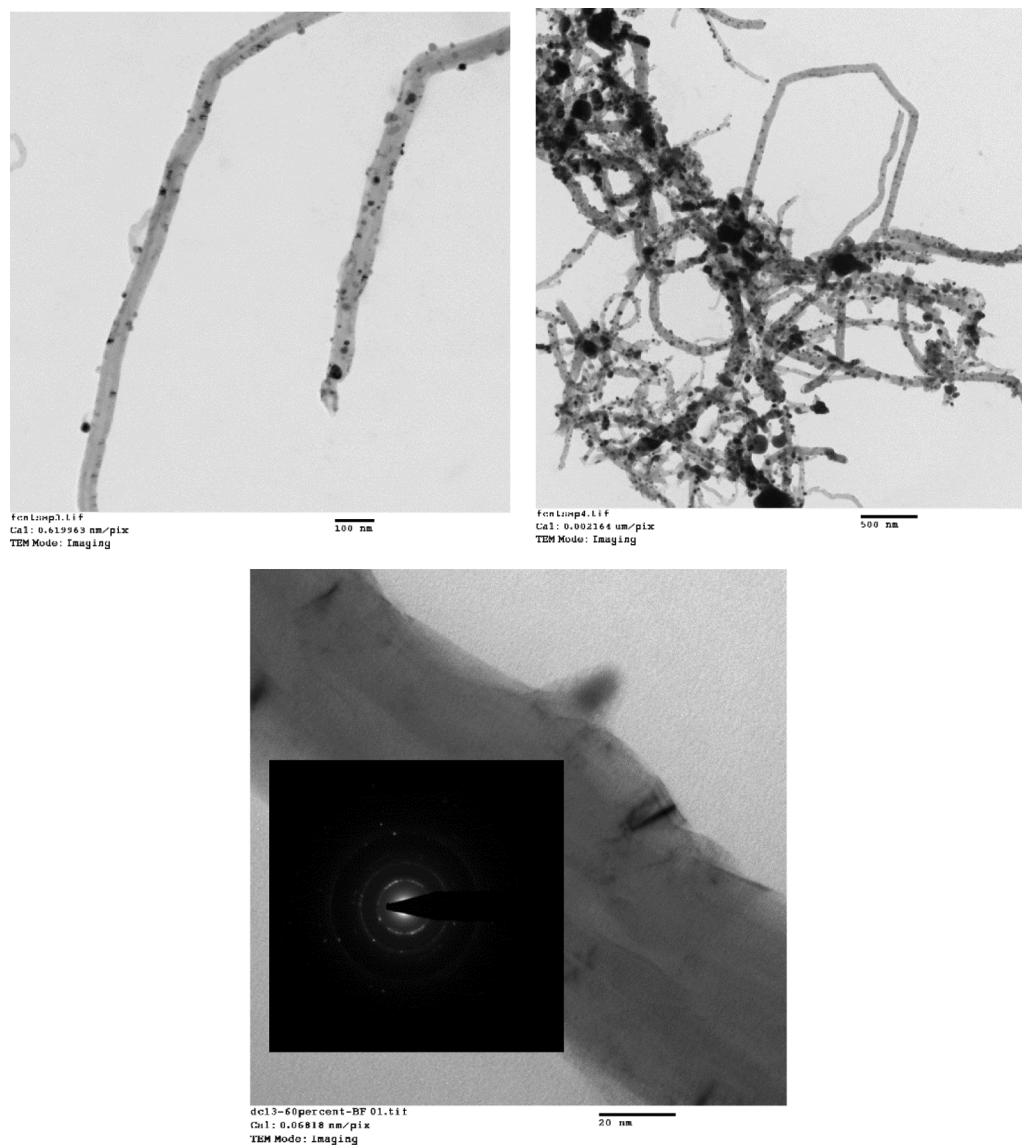


Fig. 2. TEM micrographs of FSA-1.

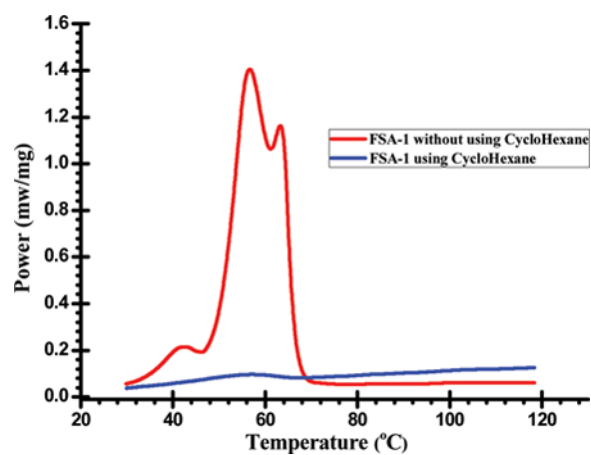


Fig. 3. Variation power versus temperature of FSA-1 samples before and after washing cyclohexane.

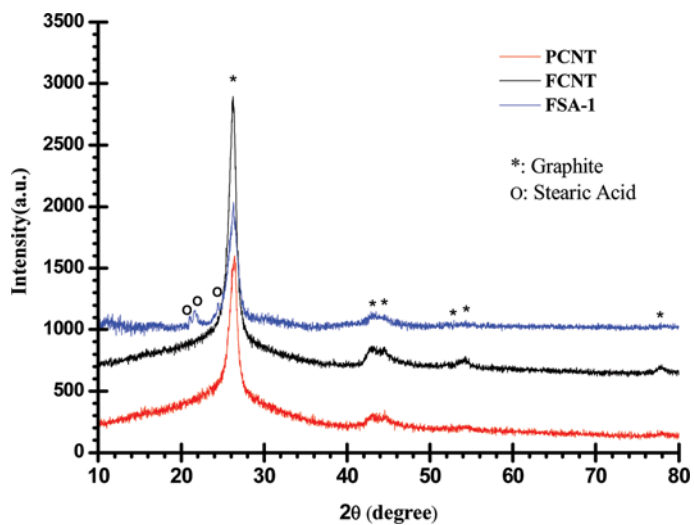


Fig. 4. XRD pattern of PCNT, FCNT, and FSA-1 samples.

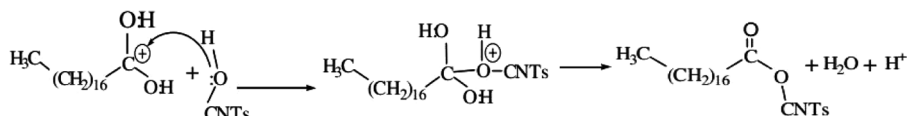


Fig. 5. Schematically esterification reaction between SA and FCNT (Chen et al. 2005).

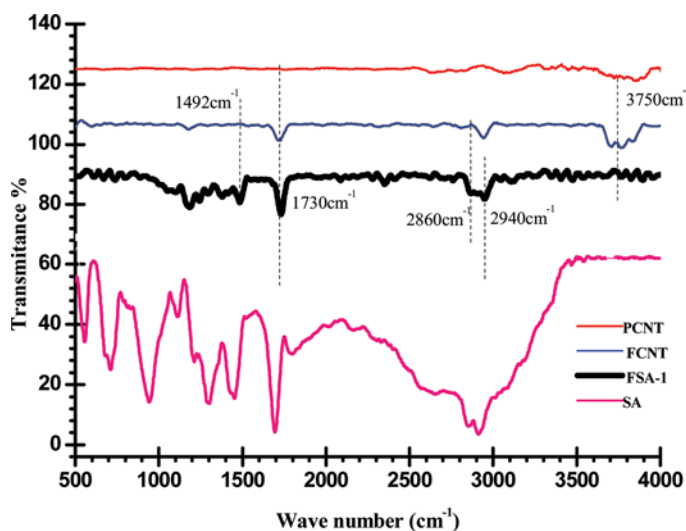


Fig. 6. FTIR spectrum of PCNT, FCNT, SA, and FSA-1.

weight loss below 400°C is related to water loss and the formation carboxyl groups, and weight loss above 400°C is related to the loss of oxygen atom tightly bonded to the surface of the MWNTs or nongraphitic carboneous species.

The two peaks for the FSA-1 samples indicate that two different types of stearate exist on the surface of FCNT. The higher temperature peak probably corresponds to a much stronger interaction surface, while the other maybe related to layers that are only physically absorbed. The chemisorbed monolayer is chemically reacted with the free

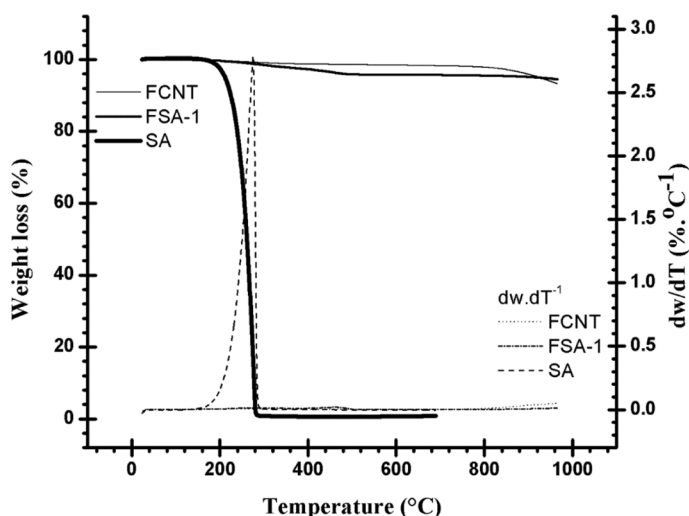


Fig. 7. Weight loss of FSA-1 and SA samples versus temperature.

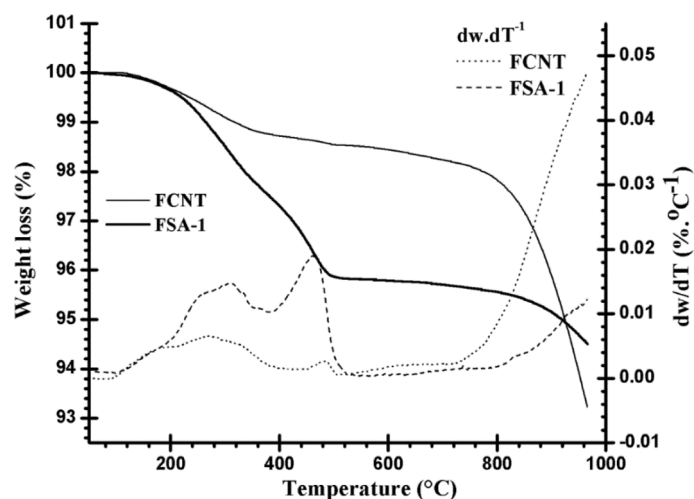


Fig. 8. Thermal degradation graph of FSA-1 and FCNT samples.

active sites of FCNT, which can be seen at the higher temperature.

Conclusion

In order to coat CNTs with SA, the wet chemical treatment was selected by using acetone as media. The results showed that the hydroxyl and carboxyl group on the surface of CNTs are significant for the esterification reaction. As well, washing with cyclohexane and chloroform completely removed the unreacted of SA from the surface of the CNTs. The round shape of SA particles homogenously deposited on the surface of CNTs with a medium diameter size of 20 nm. The results prove that the esterification reaction occurred at the surface of the FCNTs. TGA results show that about 4.3%wt SA was formed on the surface of FCNT.

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