

Accounts of Materials & Surface Research

Attempt of uniform dispersion in polymer-based nanocomposites using surface-modified single-walled carbon nanotubes

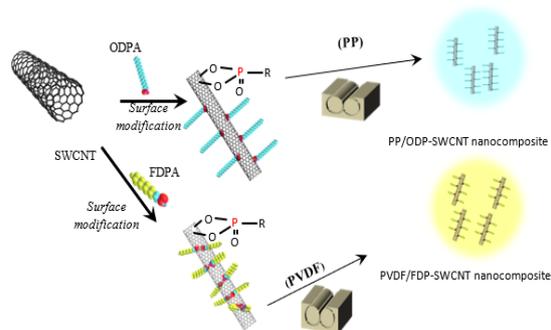
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Surface modification of single-walled carbon nanotubes (SWCNTs) was applied by long-chain phosphonic acid derivatives with non-desorbing properties. By attainment of well-dispersion of organo-modified SWCNTs in organic solvents, monolayer on the water surface of organo-SWCNT was formed from this dispersed media as spreading solution. In comparison to compounds that used in surface modification of SWCNTs by monodentate bonds, the surface modification for SWCNTs with bidentate bonds compounds leads to excellent heat resistance properties. On the polymer-based nanocomposite formation, hydrogenated and fluorinated SWCNTs could easily introduced into hydrogenated and fluorinated polymers respectively via a simple melt-compounding method. There was improvement in crystallization temperature of fluoropolymer/fluorocarbon modified SWCNTs nanocomposite in comparison to the neat polymer. In this case, the lamella thickness, the thermal degradation temperature, the crystallite size, and the mechanical properties were also improved/increased in these nanocomposites.



Keyword: Single-walled carbon nanotube; Organo-modification; Fluorinated phosphonic acid; Bidentate Long-Chain Phosphonic Acid; polymer-based nanocomposites

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Attempt of uniform dispersion in polymer-based nanocomposites using surface-modified single-walled carbon nanotubes

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1. Introduction

A carbon nanotube (CNT) consisting of carbon atoms arranged in one or more cylindrical layers, in a hexagonal tiling pattern by covalent bonds, and form a hollow tube up to a few hundred nanometres. A single-wall carbon nanotube (SWCNT) has a single cylindrical layer of atoms, consist of a single molecule, with diameter in the range of a nanometer. CNTs at the molecular and the macroscopic scales are found to present the ability of strong interaction with molecules by non-covalent interaction.¹⁻⁴ As a result, the non-covalent chemical functionalized of CNTs with various polymers has been used in creating dispersions for improving interactions between the CNTs and composite matrices.⁵⁻⁹

The high performance of carbon fiber-reinforced plastics (CFRPs) and their various applications make many researches and projects have been executed to enhance properties of the composite materials.¹⁰⁻¹² CFRPs with thermoset matrices have some limitations like as poor recyclability and low impact resistance. However, CFRPs with thermoplastic matrices, such as polypropylene (PP), polyethylene (PE), polyamide (PA), etc. have attention because

it has not requirement curing and its less toxic, in addition to more recyclable.¹³⁻¹⁵ Therefore, to enhance the properties of these fiber-reinforced composites, many surface modifications processes have been done like as nanoparticles modification, acid treatment, and nanofiller coating, and so on.¹⁶⁻³⁰

Beom-Gon Cho et al, fabricated polyamide 66(PA66)/ carbon fiber (CF)/acyl chloride-functionalized graphene oxide (AGO)-CNT composites by interfacial polycondensation. In this case, high mechanical properties were obtained, and these improvements may be due to hydrogen bonding and well-dispersion.³¹

Hirayama et al, created crystalline polymer/clay nanocomposites using sustainable sepiolite as a material with similar shape to the SWCNTs, this clay was modified using phosphonate derivative. This surface modification of sepiolite using phosphonate derivative that form bidentate bond with clay surface improved the desorption temperature and make the chance for nanocomposite preparation high and possible by simple melt-compounding. Sepiolite achieved well nano-dispersed state, the mechanical properties and the crystallinity were improved/increased in the corresponding nanocomposites.^{32,33}

Abiko et al, attained the dispersion of organo-modified SWCNTs in organic solvent by the modification of the CNTs surface with bidentate long chain phosphonic acid leading to excellent heat resistance, and its structural characterized by monolayer formation on the water surface. It is clarified that the great added value for using heat-resistance bidentate surface modification for SWCNTs.³⁴

Baek et al, showed the dispersion of CNTs in polycarbonates using the solvent dispersion method. In comparison to neat polycarbonate, the CNT-polycarbonate showed improvement in thermal stability and mechanical properties. Also, the carbon fiber/polycarbonate-CNT composites present higher interlaminar shear strength (ILSS) compared to carbon fiber/ poly carbonate composites.³⁵⁻³⁸

A synergistic effect of combining two nanofillers (e.g., CNTs and graphene) has previously been reported in various materials.³⁹⁻⁴⁵ Dul et al, developed carbon-based thermoplastic materials with electrically conductive properties and good mechanical properties. These nanocomposites depended on co-supporting network of hybrid graphene nanoplatelet (GNP) / CNTs nanofillers and exhibits higher values than single-filler nanocomposites.⁴⁶

CNTs play a nucleating agent's role in nanocomposites leading to hybrid *shish-kebab* structures, which consists of *shish* as long central fiber core, surrounded by *kebab* as periodically attached along the *shish*.⁴⁷ Several studies showed the nucleation effect of CNT as a nucleating agent and improvement the degree of polymer crystallinity. CNT affect the morphology at crystallization of polymers in thin films lower

than in the bulk because of the effect of substrate interactions. Hernandez et al, reveal that when the agglomerates be bigger, these agglomerates led to more effective nucleating points in comparison to SWCNTs isolated bundles during crystallization process.⁴⁷⁻⁶⁰ Also, CNT dispersion in a polymer depends on function of the mix tubes method with the polymer. An evidence for SWCNTs role as nucleating agent is inducing the polymer crystallization in the thinnest films in poly (butylene terephthalate) (PBT) / SWCNT nanocomposites.⁴⁷ In this case, due to the aggregation of CNTs based on their strong van der Waals interactions, their solubility was decreases and their dispersion in the solvent was limited.^{61,62} Therefore, covalent or non-covalent surface modification of CNTs is the main stream now.^{61,63} However, covalent surface modification changes the intrinsic mechanical properties of CNTs.^{64,65}

Kohei et al, showed the reduction in the young's modulus of CNT-based materials by increasing the functionalization of CNTs with oxygens.⁶⁶ Therefore, non-covalent functionalization is the choice to retain the properties of CNT.⁶⁷ Cellulose is considered a promising polymer in the field of non-covalent functionalization.⁶⁸⁻⁷¹ However, there are reduction in strength due to CNTs agglomeration and weak dispersion. Shishehbor et al, reported that using CNTs-wrapped cellulose could produce tough, strong, and stiff nano paper.⁷²

Miyako et al, developed a method for dispersion of SWCNTs in a poly(dimethylsiloxane) (PDMS) matrix by non-covalent complex formation using bovine serum albumin (BSA) as a protein and phospholipid. The results of this study

showed that phospholipid-bovine serum albumin functionalized SWCNT complex (PL-BSA-SWNT) was dispersed very well in a PDMS matrix in contrast to non-functionalized SWCNTs.⁷³

Kleinschmidt et al, reported the functionalization of CNTs by acid treatment, amination and O₂ plasma treatment. This method leading to occurrence of large amount of interaction sites on the CNTs. This functionalization afforded well nanofillers for nanocomposites. Ionic liquid IL, 1-*n*-butyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide (BMImNTF₂) with functionalized CNTs provided high performance nanocomposites of epoxy/CNTs. The functionalization process of CNTs by acid treatment, O₂ plasma and amination improved mechanical properties of the nanocomposite and its T_g in comparison to neat resin. On the other side, the functionalization process of CNTs by acetone and sodium dodecyl sulfate (SDS) weakened the CNTs leading to lowered T_g for nanocomposites.⁷⁴

2. Morphological characterization of organo-modified SWCNTs by method of organized molecular films

By the surface modification of a SWCNTs with reacting surfactant on the hydrophilized surface, it is investigated CNTs as a monolayer on the water surface and their Langmuir-Blodgett (LB) films.^{75,76}

To attempt confirmation of the organo-modification, the surface pressure-area (π -A) isotherms were measured in addition to thermogravimetry (TG). TG was measured at a heating rate of 10 °C·min⁻¹ in the atmosphere of N₂ Gas. Figure 1 shows π -A isotherms of octadecyl phosphonic acid

(ODPA), 1*H*, 1*H*, 2*H*, 2*H*-perfluoro-*n*-decylphosphonic acid (FDPA), ODP-SWCNTs and FDP-SWCNTs, respectively. These data show a stable monolayer formation of ODP- and FDP-SWCNTs and their difference to the corresponding behavior of modifier-molecules alone. Although the organo-modified SWCNTs by different surfactants with monodentate bonds have previously been studied,^{34,75} these results indicate that it can be suppressed the desorption of the modified chain by bidentate bonding with long-chain phosphonic acid.

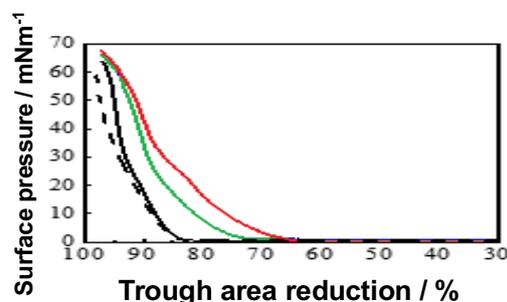


Figure 1. π -A isotherms of ODPA (—), FDPA(---), ODP-SWCNTs(—) and FDP SWCNTs(—).

Figure 2 shows atomic force microscopic (AFM) images of monolayers on solid substrate of ODP- and FDP-SWCNTs. A fibrous morphology of the single-particle layer on the solid has been confirmed. This fibrous morphology appears to indicate significant aggregation both laterally and vertically. This phenomenon may indicate that the morphological development of SWCNT,

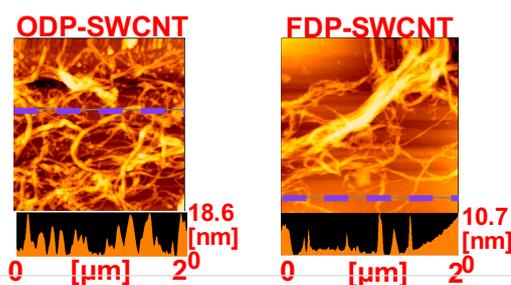


Figure 2. AFM image of a monolayer on a solid ODP-SWCNTs and FDP-SWCNTs.

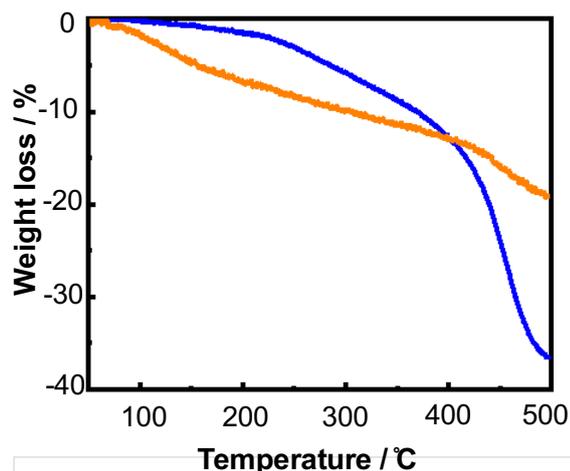


Figure 3. TG curves of ODP-SWCNTs (—) and FDP-SWCNTs (—).

which is highly aggregation tendency, was promoted during the natural drying of single-layer film transfer.

By analysis of in-plane X-ray diffraction, it has been proven that the state of modified chains of ODP-SWCNTs was similar to amorphous, while the modified chain of FDP-SWCNTs showed crystalline packing. At the same time, confirmation of D and G band shifts of the Raman spectrum indicated the presence of SWCNTs in prepared LB film and indication to successful of organo-modification process.⁷⁵ Especially, in the case of FDP-system, the G/D ratio was clearly

improved as the number of highly integrated parts increased, in contrast to ODP-system.⁷⁵

3. Thermal behavior of polymer-based nanocomposites with organo-modified SWCNTs

Thermal degradation, melting and crystallization behaviors are essential parameters to understand thermal properties of the nanocomposites.⁷⁶ Figure 3 shows TG curves of ODP- and FDP-SWCNTs, respectively. The high weight loss rate of modified chain in the hydrocarbon-modified SWCNTs reflects that the modification rate is high. Slightly weight loss occurred at 100 °C due to hydrophilic functional groups from SWCNT surface desorption. On the other hands, the desorption of the modified chain itself was indicated at 400 °C because of existence of a strong bidentate bond between the modifier and SWCNTs surface. This tendency was almost same at both organo-modified SWCNT types.^{34,76} As the result, it was found that the nanohybridization of SWCNTs by melt-compounding method with variety of polymers having high melting point is effective. Figure 4 shows the increasing of thermal degradation temperature of the PP

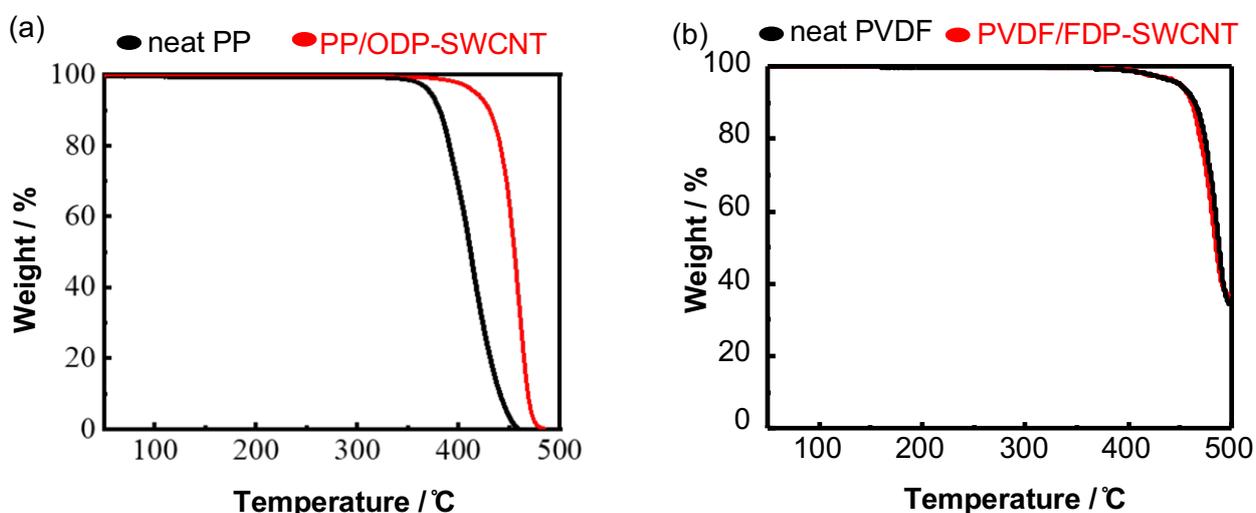


Figure 4. Thermogravimetric analyses curves of (a) hydrogenated and (b) fluorinated nanocomposites compared with their corresponding neat polymers.

system and maintaining the thermal degradation of polyvinylidene fluoride (PVDF) system. This result may be because of the affinity interaction following miscibility between the matrix polymer and the modified chain.^{34,76}

Figure 5 shows thermograms of differential scanning calorimetry (DSC) of PP/ODP-SWCNT and PVDF/FDP-SWCNT nanocomposites in comparison to corresponding neat polymers. It is noticeable that the crystallization temperature of neat PVDF increased by nanohybridization. The phenomenon of maintenance and enhancement of melting / crystallization temperatures of fluorinated nanocomposite without significant decreasing is very characteristic (Table 1) and indicated the presence of an interaction between the matrix polymers and modified agents. In the case of nanohybridization of crystalline polymer-based composed materials including other substances/fillers without affinity and/or well-dispersibility, the crystallization temperature is often decreased. Probably, this improvement behavior is evidence of increasing the interaction with the polymer

Table 1. Changes in crystallization temperature of hydrogenated and fluorinated nanocomposites compared with their corresponding neat polymers estimated by DSC thermograms.

Materials	Onset temperature of crystallization peaks (°C)
Neat PP	132.5
PP / ODP-SWCNT nanocomposite	130.7
Neat PVDF	145.9
PVDF / FDP-SWCNT nanocomposite	150.9

chain and therefore increasing dispersibility.³⁴

4. Effect of nanocomposite preparation with organo-modified SWCNTs on solid-state structure and physical properties of polymers

Table 2 shows the crystallite sizes that calculated by Scherrer formula from half-value width of the diffraction peaks from wide angle X-ray diffraction (WAXD) profiles of PP/ODP-SWCNT and PVDF/FDP-SWCNT nanocomposite in comparison to corresponding neat polymers.³⁴

From Table 1 and 2, it is noticeable that the crystallization temperature shifts to the

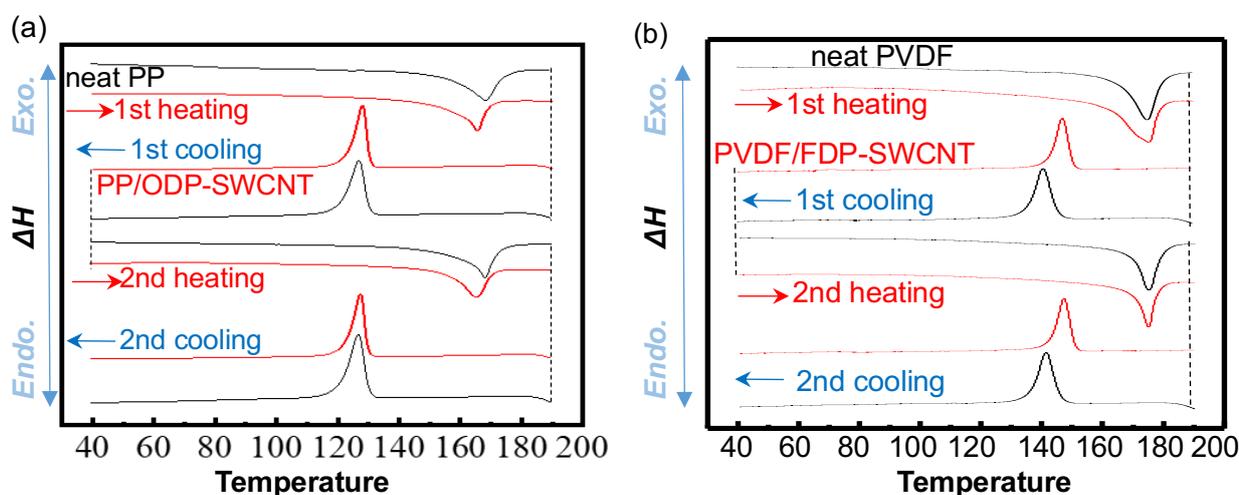


Figure 5. DSC thermograms of (a) hydrogenated and (b) fluorinated nanocomposites compared with their corresponding neat polymers.

Table 2. Crystallite sizes of hydrogenated and fluorinated nanocomposites compared with their corresponding neat polymers using the Scherrer formula.

Materials	Crystallite size (Å)
Neat PP	D_{040} : 246.4
PP / ODP-SWCNT nanocomposite	D_{040} : 258.9
Neat PVDF	D_{110} : 234.4
PVDF / FDP-SWCNT nanocomposite	D_{110} : 237.9

high temperature side and the specific crystallite size increases (PP system D_{040} , PVDF system D_{110}) by nanocomposite preparation. These results simultaneously reflect an increase in lamella thickness along the *c*-axis direction and an increase in the crystallite size in the *ab*-plane. Therefore, it finds that existence of nanofillers does not obstruct crystal growth. On the contrary, increasing in crystallite size was indicated by nanohybridization.³⁴

By the analysis of small-angle X-ray scattering (SAXS) of PP/ODP-SWCNT and PVDF/FDP-SWCNT nanocomposites, in comparison to corresponding neat polymers, it was indicated that improvement of lamella thickness due to the nanohybridization.⁷⁵ These results were predicted as an existence of the interaction between the ends of modified-chain and the polymer chain essential to occur the nucleation effect and resultant heterogeneous nucleation.

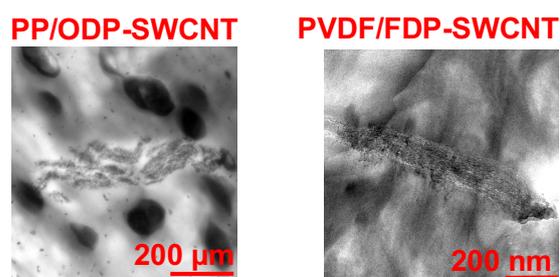
Table 3 shows the values of young's modulus of PP/ODP-SWCNT and PVDF/FDP-SWCNT nanocomposites in comparison to corresponding neat polymers. It is noticeable that the mechanical properties are almost maintained in the PP system and enhanced in the PVDF system. These-like enhanced or maintained physical properties

Table 3. Young's modulus of hydrogenated and fluorinated nanocomposites compared with their corresponding neat polymers estimated by S-S curves.

Materials	Young's modulus [MPa]
Neat PP	710.3
PP / ODP-SWCNT nanocomposite	697.6
Neat PVDF	1133.8
PVDF / FDP-SWCNT nanocomposite	1454.6

might be caused by the miscibility between the modified chain and the polymer chains.³⁴ From previous study,⁷⁷ it is concluded that phosphonate derivative with bidentate bonds and its free substitution at the other end can help in the imparting miscibility with the matrix polymers. In addition, it can help in suppression of desorption of modified chains at high temperature and help affinity of nanohybridization to be occurred. This tendency had also been confirmed in the previous study.⁷⁷

Figure 6 shows transmission electron microscopic (TEM) images of hydrogenated and fluorinated nanocomposites. In hydrogenated nanocomposites, ODP-SWCNT was used as nanofillers for PP matrix, and FDP-SWCNT was used as nanofillers for PVDF matrix in fluorinated nanocomposites. At present, although it has not been possible to achieve well-dispersed state, SWCNTs

**Figure 6.** TEM images of (a) hydrogenated and (b) fluorinated nanocomposites.

which were difficult to introduce into polymers in the first place, have been nanohybridized with a certain minute size. Near future, an academic paper on a technology that succeeded in achieving well-dispersion will be published.

5. Conclusion

This review details previous studies involving various approaches for dispersion of surface-modified SWCNTs in polymer-based nanocomposites. Surface modification of SWCNTs was applied by long-chain phosphonate derivatives with bidentate bond leading to non-desorbing and excellent heat resistance properties. As shown in this review, hydrogenated and fluorinated SWCNTs could easily introduced into hydrogenated and fluorinated polymers leading to improvements in physical properties of polymer composites.

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