Preparation of Polymer Nanocomposites Containing Multiwall Carbon Nanotubes Functionalized by Chloroform Plasma

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Abstract

The carbon nanotubes (CNTs) can more efficiently enhance the polymer properties than the other nanofillers due to their unique physical and chemical properties. However, the good dispersion of carbon nanotubes into the polymer matrices is challenging because the CNTs tend to form bundles and agglomerate due to strong van der Waals interactions between the nanotubes. The functionalization of carbon nanotubes can help solve this problem and lead to the good dispersion of CNTs in polymers. In this study, the multiwall carbon nanotubes (MWCNTs) were functionalized using dielectric barrier discharge plasma in helium saturated with chloroform. Then, the functionalized MWCNTs were used to prepare the polymer nanocomposites with a good dispersion state of nanotubes. Fourier transform infrared spectroscopy (FTIR) results showed that the MWCNTs' surfaces are functionalized with the chlorinated group due to exposure of the MWCNTS to the plasma. Moreover, the optical microscopy images and measured rheological properties of the nanocomposites indicated that the plasma-functionalized MWCNTs are better distributed into the polymer matrix than the unfunctionalized MWCNTs. This confirmed that the plasma functionalization enhances the interactions between the MWCNTs and the polymer matrices.

Keywords: Polymer nanocomposites, Carbon nanotubes, Functionalization, Plasma

Introduction

Composites are solid materials comprising two or more components. The properties of the composite material should differ from each component's properties. Composites usually include a continuous phase, primarily a polymer, ceramic, or metal, and a dispersed phase, such as fiberglass, carbon particles, silica powder, and clay [1, 2]. The recent advances in nanotechnology have led to the emergence of a new class of composites known as nanocomposites. According to a widely accepted definition, nanocomposites are composite materials containing at least one dispersed component with at least one nanoscale dimension. Adding these nanocomponents, called nanofillers, as a dispersed phase (or reinforcing phase) to materials like polymers as a continuous phase leads to composites with excellent properties and diverse potential applications [3, 4].

Polymeric nanocomposites are one of the most important subclasses of nanocomposites, which have attracted much attention and have been the focus of many pieces of research [5, 6]. Some polymeric nanocomposites have been commercialized and used in industry [7]. In polymeric nanocomposites, the continuous phase, called the matrice phase, is a polymer, and the dispersed phase, or reinforcing phase, comprises one or more mineral nanofillers [8]. Polymers have diverse applications in industry owing to their unique properties, such as facile synthesis, lightness, and flexibility. However, polymers have lower strength, chemical, and thermal stability than metals and ceramics and are usually nonconductors. Nanofillers like activated carbon, nano-silica, nano-clay, carbon nanofibers, and carbon nanotubes can be added to these materials to enhance polymers' mechanical, electrical, and thermal properties. These nanoscale fillers can reinforce polymers much better than common fillers due to their large specific surface area and aspect ratio [9, 10].

Carbon nanotubes (CNTs) are one of the most important nanofillers that can be employed as an ideal reinforcing nanocomponent to synthesize multi-task polymeric nanocomposites [11]. Compared to other nanofillers, CNTs can improve polymers' properties more effectively due to their excellent properties and high length-to-diameter ratio [12, 13].

Generally, CNTs have great potential in many applications owing to their electrical, mechanical, thermal, optical, and chemical properties. The electronic properties of CNTs have gained particular attention. The nanometer size and completely symmetrical structure of nanotubes lead to interesting quantum effects and electronic, magnetic, and lattice properties. Numerous theoretical calculations and experimental measurements have confirmed the abnormal electronic properties of nanotubes (for instance, the quantum wire property of a single-wall nanotube, a group of single-wall and multiwall nanotubes, and semiconducting and metal characteristic of a single-wall nanotube). Since the discovery of nanotubes, these unique properties have resulted in various applications of these materials in detection, catalysis, composites, absorption, drug delivery, biology, and nanoelectronics [14].

To maximize the reinforcing effect of CNTs on polymers, they must be well dispersed in the polymeric matrix [15]. CNTs tend to aggregate and form bundles due to the strong van der Waals interactions between nanotubes, making their uniform distribution in polymeric matrix cumbersome. One crucial method to overcome this challenge is surface modification or functionalization of CNTs. Functionalization significantly improves CNTs' performance in many applications [16-18].

Several approaches are used to functionalize or modify CNTs' surface, including covalent bonding of chemical groups to the end or side wall of the CNTs, non-covalent absorption, or covering the CNTs with various functional molecules [16]. Compared to the methods based on non-covalent interactions, covalent chemical functionalization has considerable potential in adjusting CNTs' properties and is expected to encompass diverse applications of nanotubes. The standard methods for functionalizing CNTs are usually based on wet chemistry. In this method, CNTs and reactants often interact in a solution (predominantly at high temperatures). The methods based on wet chemistry usually cause damage to the graphite structure of CNTs and shorten their length. Compared to this approach, modification of CNTs using plasma is a practical low-temperature process with less pollution. Moreover, various functional groups can be grafted on the nanotubes' surface by adjusting plasma parameters such as power, applied gases, pressure, and processing time. This technique also considerably reduces the reaction time compared to other chemical methods [19, 20].

The synthesis methods of nanotube/polymer nanocomposites are primarily focused on the dispersion of nanotubes in polymer matrices [21, 22]. One of the synthesis techniques is a solution method based on phase inversion [23]. In this approach, multiwall carbon nanotubes (MWCNTs) are first dispersed in the solvent using ultrasonication. The polymer is then solved in the solvent, and the nanotubes are dispersed again through ultrasonication. Finally, water or acetone (insoluble) is added to the mixture so that the polymer is quickly precipitated and the polymeric nanocomposite is formed [24].

In this study, to sufficiently disperse the MWCNTs, they were first functionalized using a Dielectric Barrier Discharge (DBD) Plasma system at atmospheric pressure. Chloroform-saturated helium was used as the plasma gas. The plasma-synthesized polymeric nanocomposites containing functionalized CNTs were fabricated and characterized. An optical microscope was employed to measure the dispersion of nanotubes in the polymer. The rheological properties of the as-synthesized polymeric nanocomposites were determined and investigated.

Materials and Methods

A dielectric barrier discharge plasma reactor at atmospheric pressure was used to functionalize MWCNTs. Fig. 1 depicts the plasma reactor. The reactor is made of a quartz tube, with an inner diameter of 16 mm, an outer diameter of 20 mm and a height about 30 cm. It has two electrodes; the electrode connected to high voltage is made of stainless steel, and the electrode connected to the ground is a metal sheet made of stainless steel (or aluminum) wrapped around the quartz tube. First, a helium flow whose mass flow rate is controlled by a mass flow rate controller passes through a chloroform container. The helium saturated with chloroform then enters the plasma reactor, and the plasma reactor is turned on. In this study, the plasma voltage and frequency were 9 kV and 2.6 kHz, respectively. The sample was exposed to plasma for 4 min.

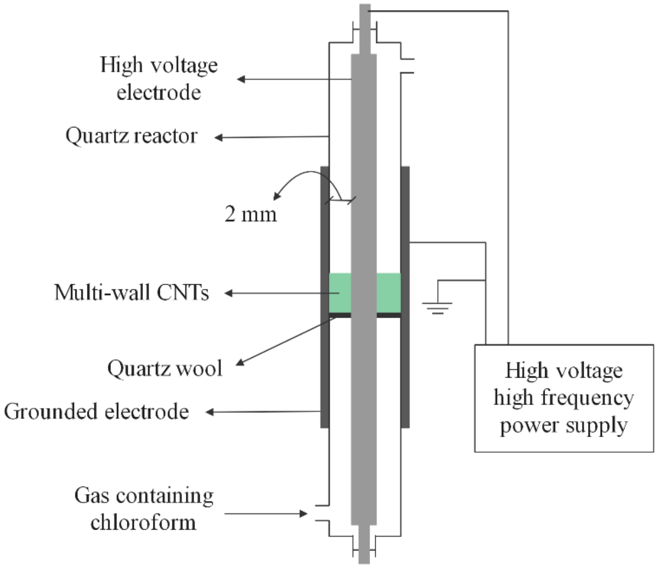

Fig. 1. Plasma set-up for functionalization of MWCNTs

Polypropylene bonded with maleic anhydride was employed as the polymer matrix to investigate the effect of plasma functionalization. Nanocomposites containing 0.5 wt.% carbon nanotubes were synthesized using functionalized and non-functionalized nanotubes. As depicted in Fig. 2, carbon nanotubes were first added to toluene to synthesize these nanocomposites and dispersed through ultrasonication. Then, a solution of polypropylene-maleic anhydride in toluene was added to the mixture. The polymer-nanotube-toluene mixture was exposed to ultrasonication for 80 min. Finally, an equimolar of acetone was added to the mixture to recover the composite. The composite was clotted as a result of phase inversion. The obtained composite gel was filtered and dried at 120 ºC. The dispersion of nanotubes in the polymer matrices was studied through optical microscopy. The nanocomposites' rheological properties were also measured.

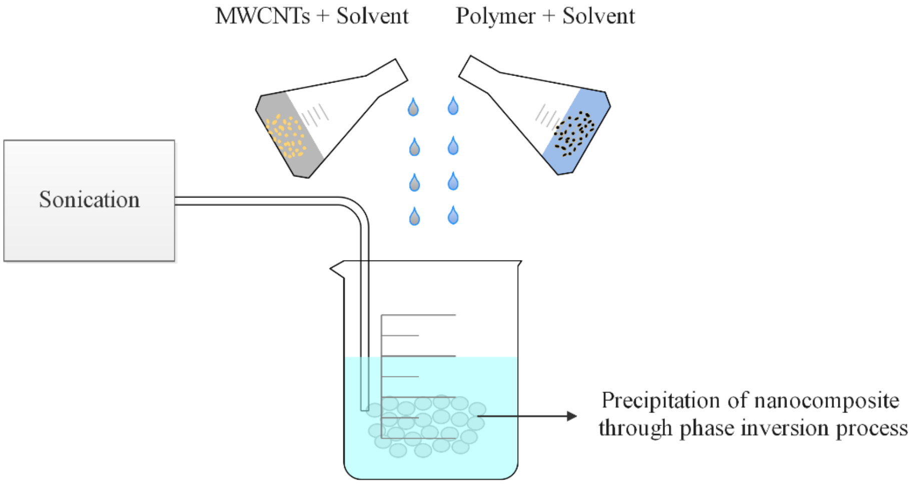

Fig. 2. Synthesis process of polymer/MWCNTs nanocomposites

Results and Discussion

The chloroform plasma was used to create chlorine functionalities on the surface of carbon nanotubes. The helium gas was passed through a chloroform-containing vessel to be saturated with chloroform. The chloroform-saturated helium entered the plasma reactor and turned the plasma system on. The plasma voltage was adjusted at 9 kV, as in all previous studies, this voltage resulted in the formation of the highest number of functional groups on the nanotubes' surface. The plasma frequency was set at approximately 2.5 kHz. The functionalization of nanotubes with chlorine groups was confirmed by FTIR spectroscopy of the nanotubes exposed to the plasma for 3 min.

The FTIR spectroscopy for non-functionalized and functionalized nanotubes is shown in Fig. 3. There are almost no peaks in the spectrum of non-functionalized nanotubes, indicating the elimination of nearly all the defects and functionalities on the surface due to annealing of nanotubes up to 1000 ºC. As can be seen from the spectrum of functionalized nanotubes, the functionalization led to a peak at 1520 cm^{-1}, which implies structural defects on the nanotubes' surface due to plasma or functionalization. There is another peak at around 657 cm^{-1}, which can be attributed to the C-Cl bonds, confirming the formation of chlorinated groups on the surface of functionalized nanotubes.

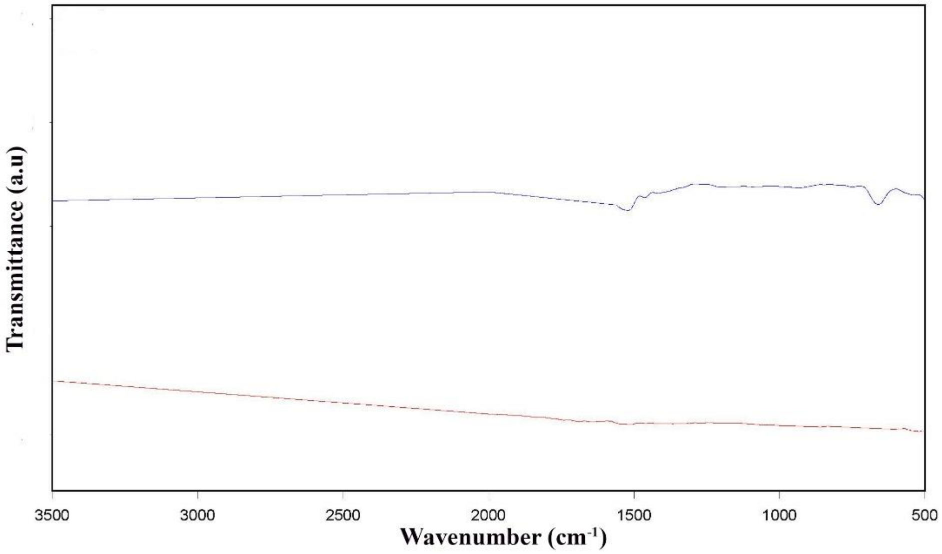

Fig. 3. FTIR spectroscopy of non-functionalized and functionalized nanotubes

Optical microscopy images of nanocomposites synthesized by non-functionalized and plasma-functionalized CNTs are shown in Fig. 4. As can be observed, the non-functionalized MWCNTs show worse dispersion than the plasma-functionalized MWCNTs. This may be due to the fact that functionalization of MWCNTs by plasma leads to an increased interaction between CNTs and polymer matrix, thus improving the dispersion of CNTs in the polymer matrix.

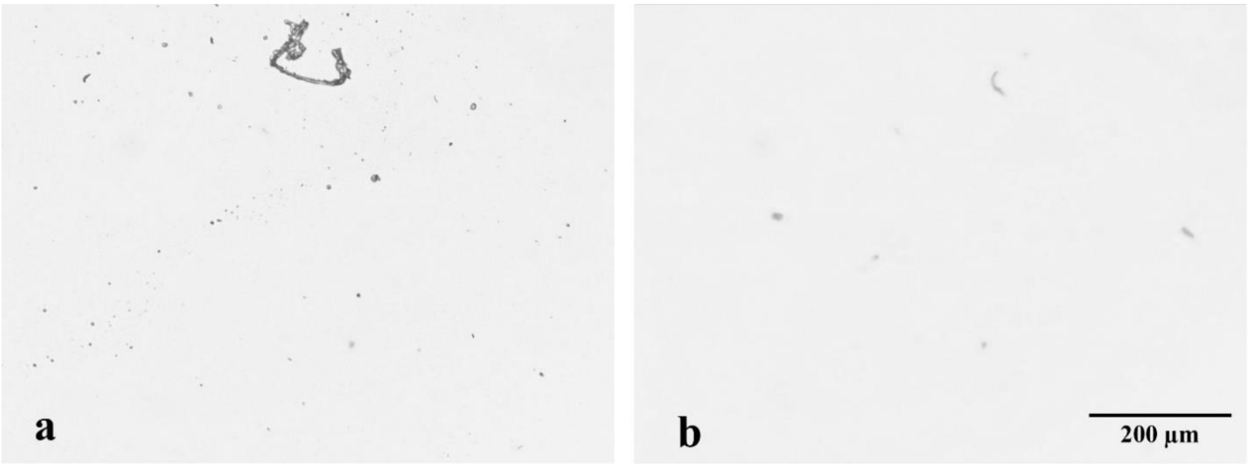

Fig. 4. Optical microscopy images of nanocomposites provided by: a. non-functionalized MWCNTs; b. MWCNTs functionalized with chloroform.

Fig. 5 plots the storage modulus of nanocomposites fabricated through non-functionalized MWCNTs and plasma-functionalized MWCNTs against frequency. Given the better dispersion of plasma-functionalized nanotubes in the polymer matrix, their resultant nanocomposites have greater storage modulus in different frequencies (especially in low frequencies). Generally, the enhanced storage modulus resulting from the inclusion of carbon nanotubes in a polymer matrix can be explained by the effect of carbon nanotubes on the microstructure of the polymer matrix. In this regard, the strong CNT-polymer and CNT-CNT may link carbon nanotubes and form a semi-lattice structure. This structure may prevent the polymer chain movements and lead to semi-solid rheological behavior. Moreover, the higher the dispersion of nanotubes in nanotube/polymer nanocomposite, the greater the storage modulus. This is ascribed to the complete formation of a nanotube network when there is a more uniform distribution of CNTs in a nanotube/polymer nanocomposite. The appearance of a complete nanotube network creates more limitations for the movement of polymer chains, resulting in more similar rheological behavior to solids [24].

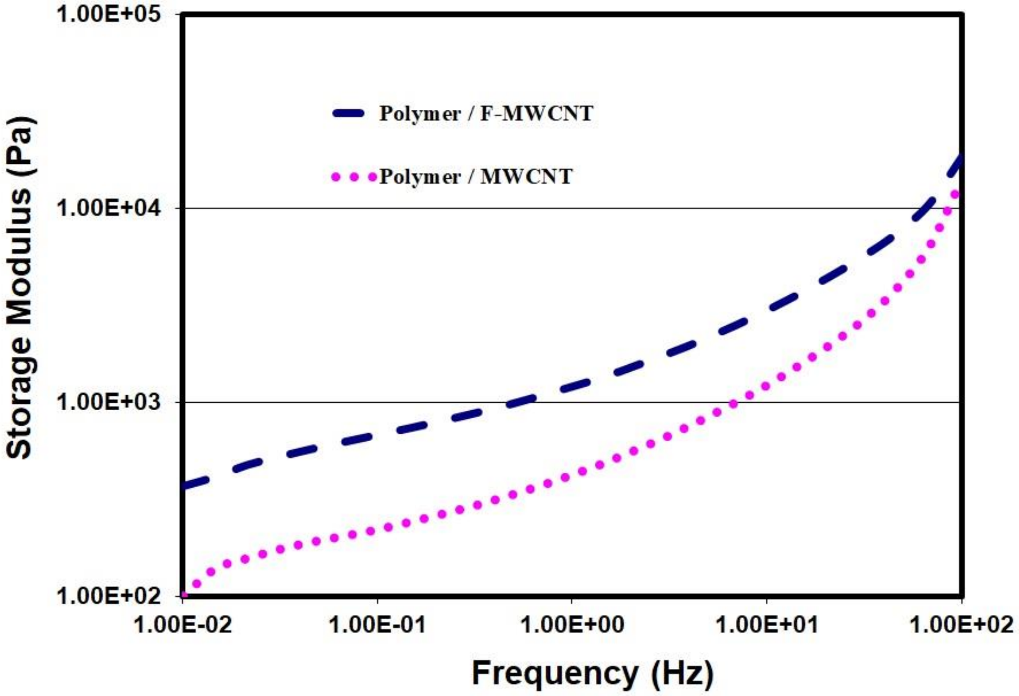

Fig. 5. The storage modulus plot of nanocomposites formed by non-functionalized MWCNTs and plasma-functionalized MWCNTs against frequency

The complex viscosity of nanocomposites based on non-functionalized MWCNTs and plasma-functionalized MWCNTs is depicted in Fig. 6. The functionalized MWCNT-based nanocomposites have higher complex viscosities in different frequencies than their non-functionalized counterparts. This implies that the plasma-functionalization of CNTs led to their improved distribution in the polymer matrix.

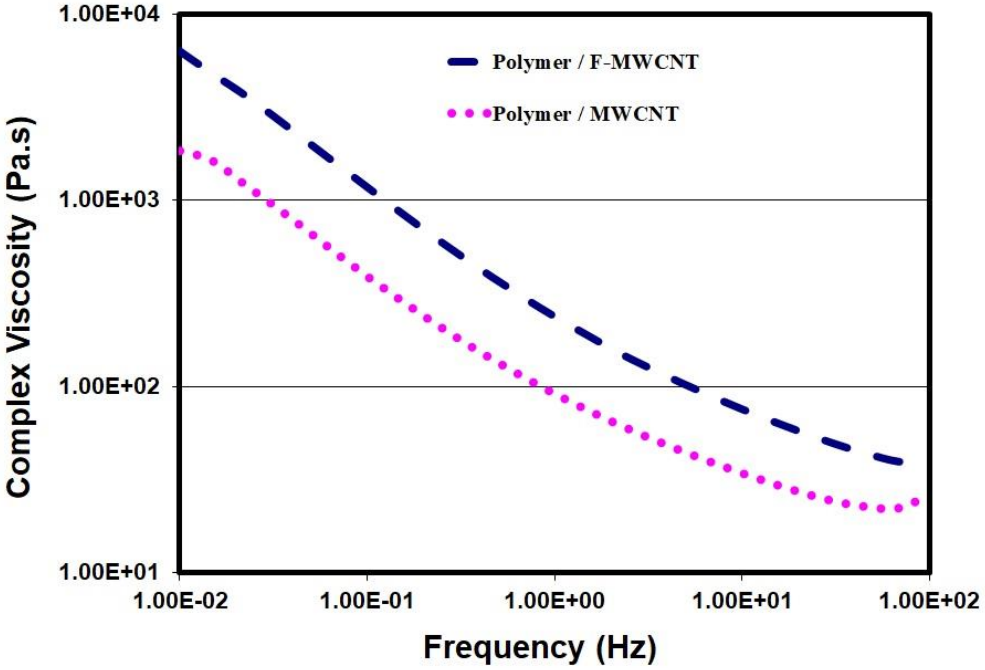

Fig. 6. The complex viscosity plot of nanocomposites based on non-functionalized MWCNTs and plasma-functionalized MWCNTs against frequency

Overall, the rheological behavior of polymers can be divided into two regions. The first region, including low frequencies, is called the Newtonian region. In this region, the storage and loss modulus heavily depend on frequency, while complex viscosity is slightly dependent on frequency. The storage and loss modulus gradually rise, and complex viscosity slowly falls linearly with an increase in frequency. In high frequencies where non-Newtonian behavior is observed, the frequency dependence is inversed. Adding nanotubes to polymers considerably affects their rheological behavior. Nanotubes increase the storage modulus and complex viscosity of nanocomposites. Also, the higher distribution of CNTs in the polymer matrix translates into their greater impact [8].

Conclusions

Due to their outstanding mechanical, electrical, and thermal properties, CNTs can be employed as the reinforcing phase in polymeric nanocomposites. However, using these nanomaterials as the reinforcing phase is accompanied by some challenges, the most serious of which is their non-uniform distribution in the matrix phase. Functionalizing CNTs can improve their distribution in the polymer matrices. Plasma-functionalization of CNTs, among other methods, is a low-temperature and practical approach with less pollution. This study used dielectric barrier discharge plasma with chloroform-saturated helium to functionalize multiwall carbon nanotubes. The properties of the plasma-functionalized CNTs-based polymeric nanocomposites were also investigated. The nanocomposites were prepared using a solution method based on phase inversion.

The results of FTIR analysis showed that chlorinated groups were grafted on the MWCNTs' surface. The optical microscopy images of the CNTs/polymer nanocomposites indicated that the plasma-functionalized MWCNTs had better distribution in the polymer matrix than non-functionalized MWCNTs. The rheological studies of the polymeric nanocomposites also proved that functionalizing MWCNTs led to an enhanced distribution of nanotubes in the polymer matrix.

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ساخت نانوکامپوزیت‌های پلیمری حاوی نانولوله‌های کربنی چندلایه عامل‌دار شده با پلاسمای کلروفرم

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چکیده

نانو لوله های کربنی به دلیل خواص فیزیکی و شیمیایی منحصر بفرد خود در مقایسه با دیگر نانوپرکن‌ها خواص پلیمرها را با بازدهی بهتری بهبود می‌دهند. اما توزیع مناسب نانولوله‌های کربنی در شبکه پلیمر چالش برانگیز است، زیرا این نانولوله‌ها به دلیل برهمکنش قوی واندروالس میان آنها تمایل به تشکیل رسوب دارند. این مشکل را می‌توان با عامل‌دار کردن نانولوله‌های کربنی مرتفع نمود. در این مطالعه نانولوله‌های کربنی چندلایه با استفاده از پلاسمای هلیوم اشباع شده با کلروفرم عامل‌دار شدند. سپس، نانولوله های کربنی چندلایه عامل‌دار شده برای تولید نانوکامپوزیت‌هایی با خاصیت توزیع مناسب مورد استفاده قرار گرفتند. نتایج طیف‌سنجی تبدیل فوریه فروسرخ نشان داد که سطح نانولوله های کربنی چندلایه با قرارگرفتن درمعرض پلاسما با گروه عاملی کلرینه عامل‌دار شده‌اند. همچنین تصاویر میکروسکوپ نوری و خواص رئولوژیک نانوکامپوزیت‌ها نشان داد که نانولوله‌های کربنی چندلایه عامل‌دار شده در قیاس با نانولوله‌های عامل‌دار نشده به طور یکنواخت‌تری در شبکه پلیمر توزیع شده‌اند. بدین ترتیب عامل‌دار کردن با پلاسما موجب بهبود برهمکنش بین نانولوله‌های کربنی چندلایه و شبکه‌های پلیمری می‌گردد.

واژه‌های کلیدی: نانوکامپوزیت‌های پلیمری، نانولوله‌های کربنی، عامل‌دار کردن، پلاسما