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Research Paper

Statistical analysis of the parameters influencing the mechanical properties of layered MWCNTs/PVC nanocomposites

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ABSTRACT: In this paper, a new method is proposed for the production of MWCNTs/PVC (multi-walled carbon nanotubes/ polyvinyl chloride) nanocomposites. In this method, a spray is used to produce layers of carbon nanotubes within a PVC matrix. Various parameters influence the production of the nanocomposite and its mechanical properties. These parameters are studied separately and the effect of each of parameter is calculated. All of the results of the statistical methods are obtained from experimental tensile testing. Results indicated that the most important parameter associated with constituents is the weight percent of carbon nanotube while the most important parameter associated with production is the mold surface temperature. The interaction effect of the two ultimately effective parameters on each other is also analyzed, and the relevant diagrams of the Young modulus and the ultimate tensile strength are prepared as well. Values of the Young modulus and the ultimate tensile strength are obtained for different weight percent values of the carbon nanotube.

Keywords: *Layered nanocomposite; Mechanical properties; MWCNTs; Statistical analysis; Spray method.*

INTRODUCTION

The increasing technological advancement and development of special applications have stressed the need for production of new materials with special properties. Nanocomposites are among the newly invented materials that address this need. Production of nanocomposites is aimed at utilizing the properties of several materials simultaneously. Polymers nanocomposites are among the most commonly used materials in nanocomposites in recent years. The reason for this use of polymers is that production of polymer nanocomposites is easier than the production of other nanocomposites. So far, various articles have reported different methods of producing carbon- nanotubes / polymer nanocomposites. Primary studies on the melt compounding of polymer with carbon nanotubes produced by the electric arc discharge method with polymer were carried out by Jin *et al*. [1]. In this work, MWCNTs produced by arc electric discharge were dispersed in chloroform by sonicating for 1 h. The chosen polymer, polyhydroxy-aminoether (PHAE) was then dissolved in the MWCNT solution. The suspension was then poured into a Teflon mold and then dried overnight in a fume-hood. Using this method, high loading levels of up to 50% wt and reasonably good dispersions were achieved. In most of the subsequent studies, little variation was used. The first study on nanotube reinforcement of solution based composites was by Shaffer and Windle [2] in 1999. They chemically dispersed a modified MWCNT in water. The resulting solution was carefully mixed with polyvinyl alcohol (PVA) in water to disperse the composite. The mixture was poured into a mold to produce films with a weight percentage of 60% of the nanotubes. They performed measurements on MWCNTs/PVA films and observed an increase in the storage modulus of polymer from 6 GPa to 12 GPa for the nanocomposite; however, little reinforcement was observed. Because better results were observed above the polymer glass transition temperature, it is easier to reinforce softer matrices. Shortly afterward, Qian *et al.*

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[3] used ultrasonic techniques to disperse MWCNTs in toluene. They combined the dispersed MWCNTs with a polyester (PS) solution. Finally, another sonication step was performed before pouring the mixture into the mold, to create film. This method has been applied and tested subsequently by many groups [4, 5]. For example, initiation of crack formation of such films was monitored using a TEM. Additionally, the appearances of cracks were found to be bridged by nanotubes. When the cracks reached widths of 800 nm, the nanotubes were observed to either fracture or pull out of the matrix. Potschke *et al.* [6] combined masterbatches of MWCNTs in polycarbonate (PC) with pure PC at 260 ^{oC} in a micromixer. Test samples were extruded in a circular mold. Extrusion was also used by Gorga and Cohen [7]. Meincke *et al.* [8] mixed polyamide 6 (PA6), ABS and MWCNTs in a twin screw extruder at 260 ^{oC}. Another example of the application of this method was described by Tang *et al.* [9]. Very good dispersions were observed using a TEM. In some cases, shear mixing can be difficult to perform because the carbon nanotubes tend to stick to the walls of the mixer. To overcome this problem, a combination of solution and melt techniques can be used. Coleman *et al.* [10] used ultrasonic treatment to disperse catalytic MWCNTs in a polyvinyl alcohol (PVA) and water solution. They studied the produced nanocomposite and observed a significant increase in the Young's modulus from 1.92 GPa to 7.04 GPa in a volume fraction of 0.6%wt MWCNTs (diameter of 15 nm). Ruan *et al.* [11] used a similar method, but used a magnetic mixer and ultrasonic bath to disperse nanotubes and reflux them to mix the nanotubes and the polymer. They performed a study on the mixing of MWCNTs and high density polyethylene (HDPE). They observed a slight increase in the modulus from 0.98 GPa to 1.35 GPa after forming the composite, and an increase in strength from 8.3 MPa to 12.4 MPa. However, interesting results were achieved on the alignment of the film via hot-drawing. By increasing the draw ratio, the modulus and strength of both polymer and composite were increased. Cadek *et al.* [12] performed nanohardness tests on films made of MWCNTs in combination with PVA and polyvinyl carbazole (PVK) using the spinning mold method. They observed that the PVA crystallinity increased linearly with increasing nanotube content, suggesting the nucleation of crystallinity due to the nanotubes. No such effect was observed for the PVK samples, suggesting that the difference in reinforcement could be related to the presence of a crystalline interface for PVA composites. This result indicates the possibility that stress transfer may be maximized by the presence of an ordered interface, as suggested by Frankland *et al.* [13]. Velasco-Santos *et al.* [5] observed a considerable increase in the modulus from 0.71 GPa to 2.34 GPa, for the PMMA mixed with a weight percentage of 1% of MWCNTs. This increase corresponds to a reinforcement rate that is equal to Cadek's value for PVA composites. However, in this work no nucleation of crystallinity was observed. This result suggests that good stress transfer can be obtained at an amorphous interface, depending on the polymer. Sefadi *et al.* [4] also performed a tensile test to analyze MWCNTs/PS nanocomposites. They observed an increase in the modulus from 1.53 GPa to 3.4 GPa with a weight percentage of 2.5%. They also reported an increase in strength from 19.5 MPa to 30.6 MPa with the same loading level. In addition, both tube fracture and pullout were observed to be in agreement with Qian's work.

The above examples were a few of the studies performed on polymer-based nanocomposites. A review of previous studies on polymer-based nanocomposites reveals that most of these studies are performed on polymers that are soluble in ordinary solvents, such as water. Therefore, the number of PVC-based research reports is very small. PVC polymer is a polymer that is only soluble in only solvents with high solubility due to its atomic bonds. Because these solvents are expensive and highly corrosive, they are not suitable for solid production of PVC nanocomposites for industrial applications. In this paper, a new method is used for the production of nanocomposites. In this method, a spraying device is used to transfer materials into the mold. The materials are arranged in layers (through layering) and are ultimately hot pressed. Carbon nanotubes between polymers are sprayed layer by layer, and thus, satisfactory dispersion and a high weight percentage are obtained. Many parameters influence the mechanical properties of the resulting nanocomposite. In this paper, the effect of six parameters on the Young's modulus and the ultimate tensile strength are investigated.

EXPERIMENTAL

Production of nanocomposites

The type of carbon nanotube used in this research was a range of multi-walled nanotubes produced using the Chemical Vapor Deposition method. The approximate lengths of the nanotubes were 10 micrometers, their diameters varied between 10 and 30 nanometers, and their purity was more than 95%. To disperse the carbon nanotubes, the 3:1 nitric acid: sulfuric acid solution was used. Nanotubes were dispersed for one hour at a temperature of 60 ^{oC} using excitation via an ultrasonic device. The solution was obtained for three different weight fractions of CNT in the composites: 1%, 3%, and 5%. The material selected for the matrix was soft PVC polymer nanocomposite used at the temperature of 185 ^{oC}.

An automatic spraying device with a hot mold on the hydraulic press was used to make the nanocomposites. The device used for producing the nanocomposites included three major parts: spray, press, and mold. The hydraulic press provides the pressure required for hot pressing. The hydraulic press has a capacity of 100 tons and it is possible to momentarily display the force and displacement by connecting it to a computer. Evidently, the amount of pressure required for the production of nanocomposites is much smaller than the capacity of device. Hence, the device is adequate for this purpose.

The second part of the device is a rectangular mold, which is warmed by three thermal element rods. Heating is performed by two 250-W thermal elements in a specific period of time. The elements can be adjusted by a control chamber. Following the initial heating of the mold, the 1500-W element is automatically activated. The mold temperature can be fixed in the temperature monitor using a thermometer installed on one side of the mold.

The third part of the device is an automatic spray with three inlet pipes for materials, wind flow and an electric valve. The required wind flow is supplied by a compressor. The spray is turned on and off by cutting or connecting the wind flow via the electric valve. Pressured materials move from the tank to the spray. The amount of the materials is determined by a screw on the spray. In addition, another bolt is also installed to adjust the spraying range (change the diameter of the spraying cone). Two stepper motors provide the movement of spray on the mold along perpendicular axes. To adjust the speed of movement of the spray on the mold, stepper motors are controlled by two separate drivers connected to a microcontroller.

PVC granules are placed in the mold, and the carbon nanotube solution is sprayed onto the molten polymer in the mold as the mold temperature reaches PVC melting point. The spray temperature for materials is adjusted such that, in the end, the bottom polymer layer becomes solid. After a layer of carbon nanotubes is formed on the polymer, the new polymer granules are added to the desired layer, and then the mold is pressed. The process is iterated to produce nanocomposites with the desired number of layers (Fig. 1). The thickness of all the produced nanocomposites was approximately 2-mm.

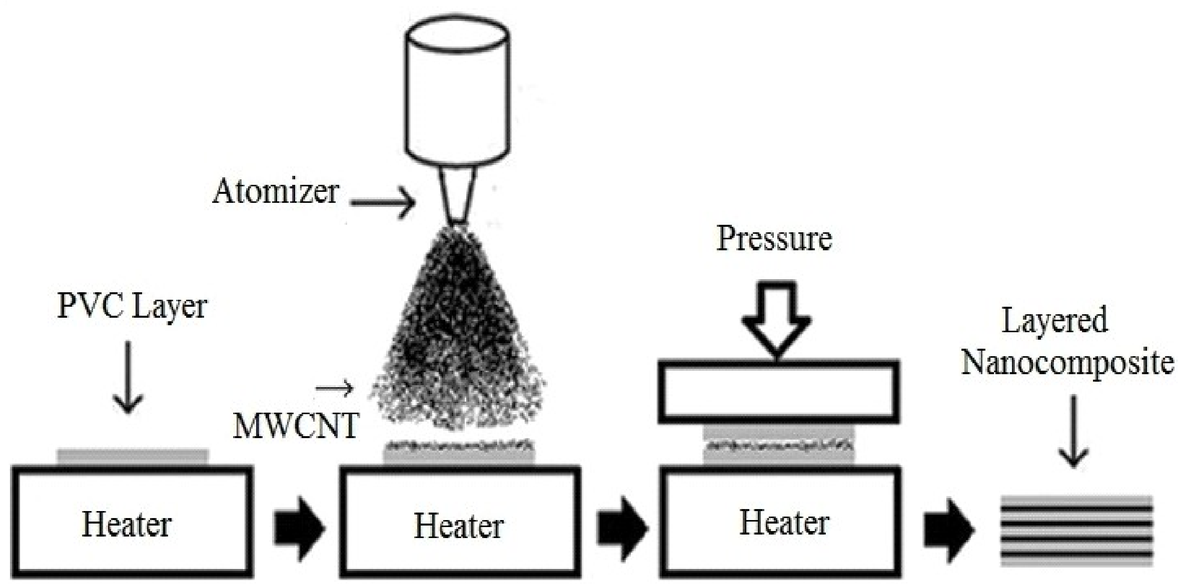

Fig. 1: Schematic illustration of the synthesis of MWCNTs/PVC nanocomposites.

Tensile testing

Samples were prepared according to the ASTM D638 standard for different number of layers (Fig. 2). A 250-kN servo-hydraulic INSTRON 8802 device was used, but for the purpose of achieving more precision, a 20-kN servo device was added to the upper jaw. The pure polymer and nanocomposite were tested three times. Tensile testing was also performed on the pure PVC polymer, the PVC nanocomposite, and single, double and triple layer carbon nanotubes. Because polymers exhibit different behaviors under pressure and temperature variations, matching of the experimental conditions with standards was attempted.

RESULTS AND DISCUSSION

Statistical Analysis of Effective Parameters

The method used for statistical control of the parameters was the Design of Experiments (DOE) method. This method was applied using Minitab 16 software. The design of experiments included a series of experiments that consciously make changes to the process input variables to measure the resulting changes caused to the process output.

In fact, the design of experiments helps to identify the process conditions and those production elements that influence the quality. The design of experiments determines the input variable to ultimately obtain the optimal and maximum results. The Minitab software presents four types of experiment designs. In this research, the factorial design type was used. The steps must be taken to create, analyze and design experiments that are similar in the case of all designs.

This section addresses enhancement of the Young's modulus and the ultimate tensile strength. Following the tests performed on important factors, it was concluded that the following six major factors influence the Young's modulus and the ultimate tensile strength: A) weight percent of carbon nanotube; B) mold surface temperature; C) solution flow rate; D) nozzle-to-mold surface distance; E) spray pressure; F) spraying diameter. First, the effect of each of the six parameters on the Young's modulus and the ultimate tensile strength was studied separately. As shown in Fig. 3(a and b), the highest influence on the Young's modulus and the ultimate tensile strength (approximately 90%) is due to the weight percent of the carbon nanotubes added to the PVC matrix. followed by the mold surface temperature (approximately 77%) and the distance of the nozzle from the mold surface (approximately 62%), which leaves the highest influence on the Young's modulus and the ultimate tensile strength.

The line drawn on the diagram shows the point at which most effects are expected to be zeroed. The impact points beyond this line result in more effective results. In addition, points on the right side of the line show factors that have a positive effect on the output.

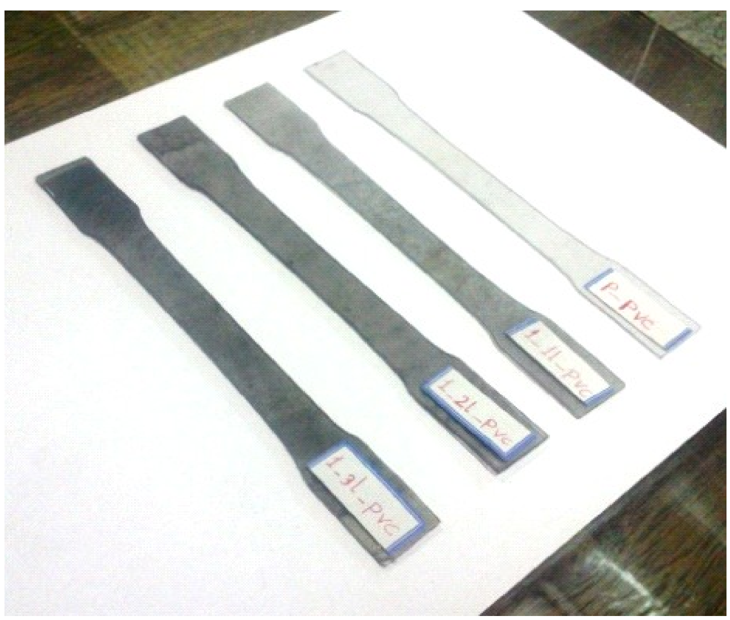

Fig. 2: Standard samples of the tensile testing.

That is, growth of the factors from the low levels to higher levels leads to the growth of the output.

According to the previous figures, the weight percent of carbon nanotubes and the mold surface temperature are two chief parameters that significantly influence the mechanical properties of the resulting nanocomposite. Hence, the interaction between these two parameters and their effect on the output are of importance. Fig. 4 depicts the diagram for the interaction between the first parameter (i.e., nanotube weight percent) and the second parameter (i.e., the mold surface temperature) on the Young's modulus and the ultimate strength. Both cases show non-parallel lines, reflecting the dependence of weight percent of carbon nanotubes on the mold surface temperature. According to the diagram, an increase in the weight percent of carbon nanotubes depends on the mold surface temperature. In other words, as the weight percent of the nanotube grows, the mold surface temperature grows as well. Evidently, the growth of the mold surface temperature leads to an increase in the Young's modulus and the ultimate tensile strength. Comparison of Fig. 4(a and b) shows that with a weight percent of less than 0.01, the gradient of the diagram for the Young's modulus is less than the gradient for the ultimate strength. However, this does not apply to high weight percentiles. That is, the ultimate strength of the nanocomposite is more dependent on the mold surface temperature than its Young's modulus with a smaller nanotube weight percent. Experimentally, attaching a carbon nanotube to polymer matrix causes defects in the polymer, whereas an increased mold surface temperature repairs the macroscopic defects of the nanocomposite. Defects caused with smaller carbon nanotube weight percent values are smaller. Because the Young's modulus obtains with less tension than the ultimate strength, the results obtain before converting microscopic defects to macroscopic defects. However, with a higher nanotube weight percent, the number of defects increase such that the same reactions, is demonstrated at lower levels of tension.

Fig. 5(a and b) shows the Scanning Electron Microscopy (SEM) image of the MWCNTs/PVC nanocomposite with 55% and 0.05% carbon nanotubes, respectively. As seen in this figure, with an increase in the weight percent of carbon nanotubes, larger defects are formed in the nanocomposite and concentration of carbon nanotubes at one point increases. Additionally, Fig. 5(c) indicates that the nanotubes were covered with matrix materials, forming bridges across the crack. Other nanotubes were broken and embedded in the matrix along the crack. The path of the crack tip was distorted because the initiation of crack propagation is more difficult. In this case the improvement in the fracture strength of the processed nanocomposites can be attributed to the bridging mechanism. The overall diameter of the MWCNTs is approximately 10 to 30 nm, whereas in some instances, a clear increase in nanotube diameter was observed and the PVC seems to wrap around the MWCNTs. The wrapping of MWCNTs is a key parameter in the improvement of the mechanical properties of carbon nanotube composites [14].

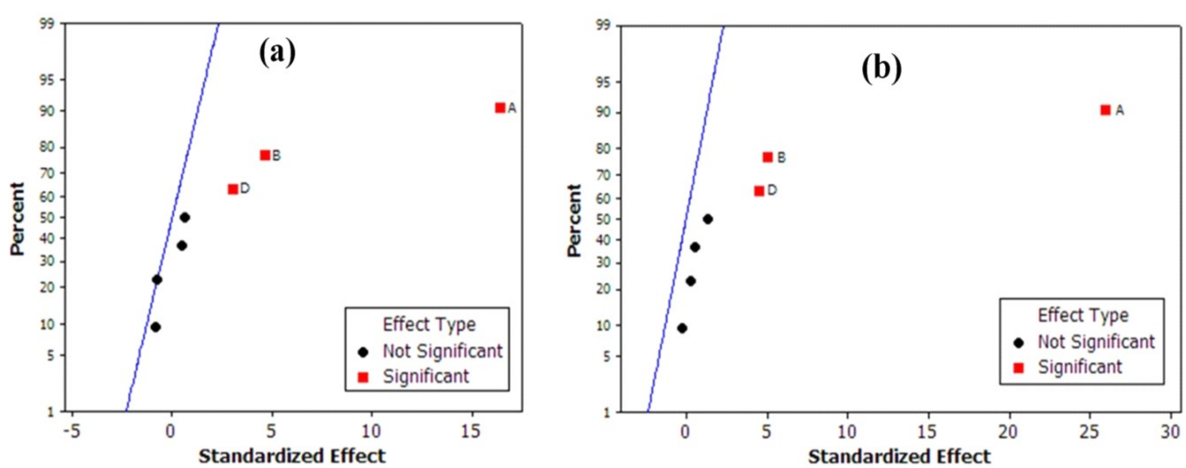

Fig. 3: The effect of different parameters on (a) Young's modulus and (b) ultimate tensile strength of MWCNTs/PVC nanocomposite.

The results obtained for different weight percent values of the carbon nanotubes are presented in Table (1). According to the results, the growth of the Young's modulus and the ultimate strength with a weight percent of approximately 10% is higher than the growth obtained with a weight percent of more than 10%. However, the conditions of six of the study parameters were ideal. If the only objective is to add to the Young's modulus and the ultimate tensile strength to reach their maximum levels, then the highest weight percent of carbon nanotubes (i.e., 55%) will be the solution.

However, the optimal weight percent of carbon nanotubes is 10% because, in an optimal condition, the use of carbon nanotubes must comply with the enhancement of the mechanical properties.

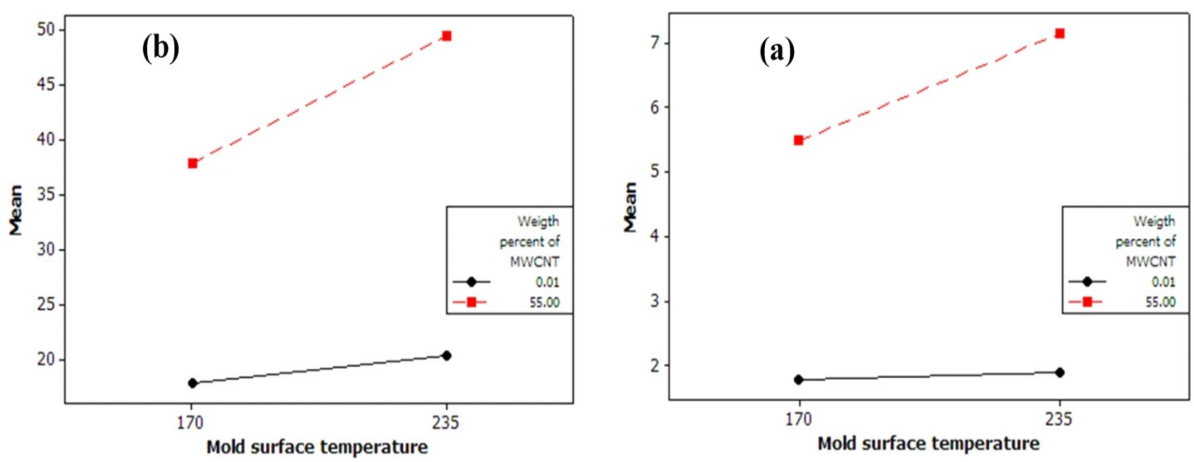

Fig. 4: The interaction effect of the weight percent on the mold surface temperature (a) average Young's modulus, (b) average ultimate tensile strength.

Table 1: Mechanical properties of nanocomposite for different weight percent values of carbon nanotubes.

Ultimate tensile strength(MPa)	Young's modulus(GPa)	Weight percent of MWCNT
15.2	0.4	0%
16.3	0.44	0.01%
18.5	0.49	0.5%
21	0.54	1%
40	1.1	10%
45	1.42	20%
56	1.68	55%

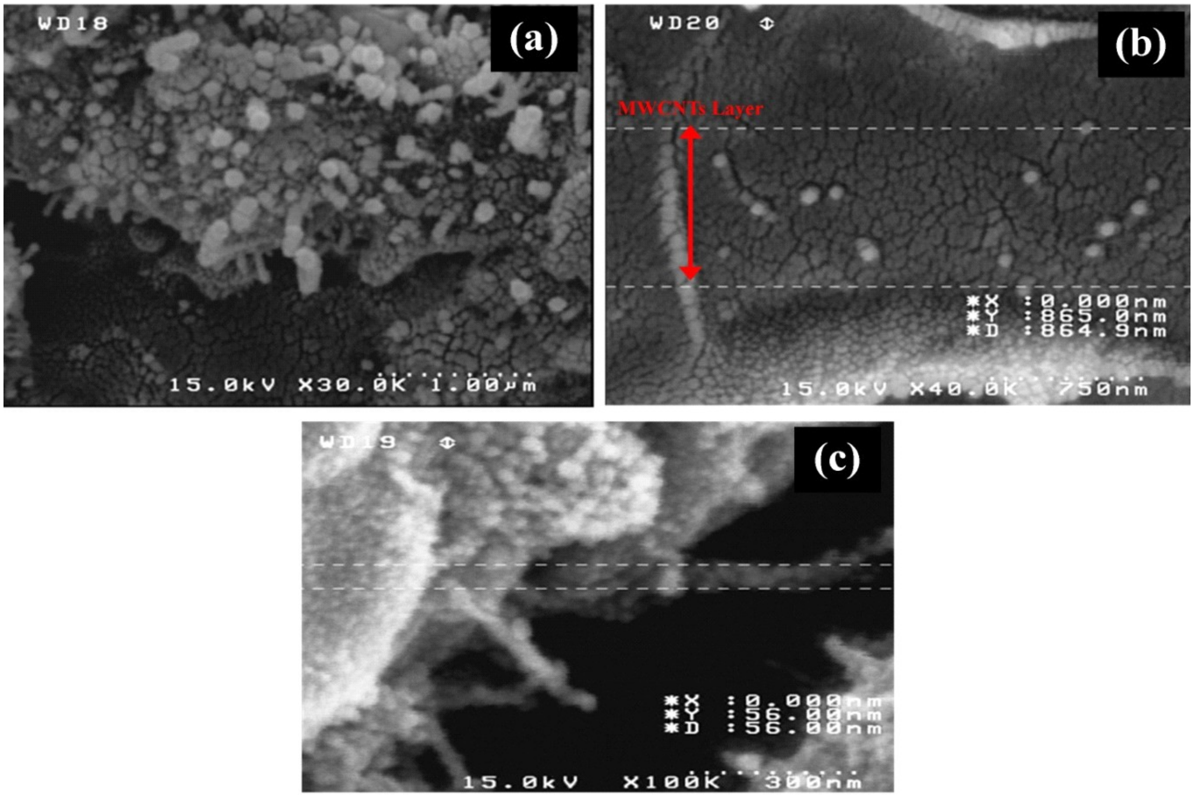

Fig. 5: SEM image of nanocomposites with (a) 55% weight percent of carbon nanotube, (b) 0.05% weight percent of carbon nanotube, (c) wrapping of MWCNT.

CONCLUSION

In this paper, the layer-by-layer spraying method was used to produce layered carbon nanotubes/PVC nanocomposite. Carbon nanotube layers were placed between the PVC layers in the hot mold using an automatic sprayer and were pressed by a hot press. Statistical analysis of six effective parameters by Minitab software indicated that the most effective parameter regarding materials is the weight percent of the carbon nanotubes whereas the most effective parameter regarding production is the mold surface temperature. The Young's modulus and the ultimate tensile strength of the nanocomposites with varying weight percent values were obtained through tensile testing. The results revealed that the optimal condition for the production of the nanocomposites using the above method is achieved with a weight percent of 10% and a mold surface temperature of 235℃. Moreover, according to the results, the weight percent of carbon nanotubes and the mold surface temperature also influence one another. That is, an increase in the weight percent of carbon nanotubes creates the need for an increase in the mold surface temperature. SEM images depict satisfactory wrapping of carbon nanotubes which leads to the improvement of the mechanical properties of CNT nanocomposites.

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