

Thermoplastic polyvinyl alcohol/multiwalled carbon nanotube composites: Preparation, mechanical properties, thermal properties, and electromagnetic shielding effectiveness

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ABSTRACT: This study uses the solution mixing method to combine plasticized polyvinyl alcohol (PVA) as a matrix, and multiwalled carbon nanotubes (MWCNTs) as reinforcement to form PVA/MWCNTs films. The films are then laminated and hot pressed to create PVA/MWCNTs composites. The control group of PVA/MWCNTs composites is made by incorporating the melt compounding method. Diverse properties of PVA/MWCNTs composites are then evaluated. For the experimental group, the incorporation of MWCNTs improves the glass transition temperature (T_g), crystallization temperature, (T_c), and thermal stability of the composites. In addition, the test results indicate that composites containing 1.5 wt % of MWCNTs have the maximum tensile strength of 51.1 MPa, whereas composites containing 2 wt % MWCNTs have the optimal electrical conductivity of 2.4 S/cm, and electromagnetic shielding effectiveness (EMI SE) of -31.41 dB. This study proves that the solution mixing method outperforms the melt compounding method in terms of mechanical properties, dispersion, melting and crystallization behaviors, thermal stability, and EMI SE. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43474.

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INTRODUCTION

Carbon nanotubes (CNTs) have been commonly used in polymer composites to improve the mechanical properties and electrical conductivity due to their characteristics of being lightweight and having high strength, high toughness, flexibility, a high surface area, and electrical conductivity.^{1–5} CNTs-based polymer composites greatly depend on the dispersion and interfacial bonding between the CNTs and the polymeric matrix. Pristine CNTs are incompatible with most polymeric materials, and their van der Waals interactions causes them to easily agglomerate in the polymer matrix and further negatively influences the mechanical properties and electrical conductivity of

the polymer composites.^{6–8} Therefore, functionalized CNTs have reduced van der Waals interactions and thus are able to disperse evenly in and are compatible with some polymeric materials. However, the functional groups in modified CNTs at the same time jeopardize their electrical conductivity.^{9–12}

PVA has extraordinary biodegradability, good water solubility, good film forming ability, toughness, barrier properties, and adhesive properties and thus can be applied in different fields, including antibacterial and biocompatible polymer composites.^{13,14} The combination of a small amount of nanocarbon materials can effectively improve the mechanical, thermal, and electrical properties of polymers. For example, Cheng *et al.* used

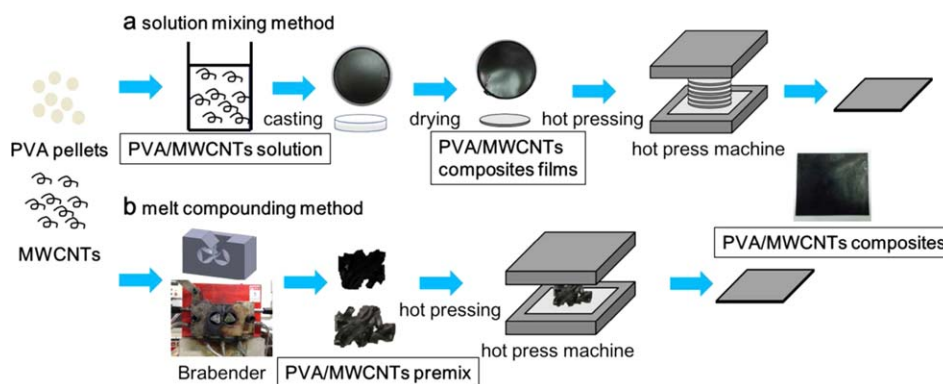


Figure 1. Two methods for preparation of PVA/MWCNTs composites: (a) the solution mixing method and (b) the melt compounding method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the solution mixing method to create PVA-grafted graphene oxide (PVA-g-GO)/PVA composites and found that the tensile strength and modulus of the PVA were increased by 88 and 150%, respectively, as a result of the combination of 1 wt % of PVA-g-GO.¹⁵ Castell *et al.* improved the dispersion of MWCNTs in PVA by using dispersants of dodecylbenzenesulfonate or polyvinylpyrrolidone (PVP). The test results indicated that MWCNTs were evenly distributed in the PVA matrix, which in turn resulted in a 12 °C increase in the glass transition temperature (T_g) of PVA/MWCNTs composites.¹⁶ In a study by Huang *et al.*, MWCNTs were immersed in a PVP solution, after which the MWCNTs coated with PVP were then distributed in a composite hydrogel. It was found that the PVP coating enabled the MWCNTs to be evenly distributed in the composite hydrogel, and thereby enhanced the tensile strength, modulus, and toughness of the MWCNT-PVP/PVA composite hydrogels.¹⁷

Due to there being a hydrogen bond between the polymer chains, the melting temperature and decomposition temperature for PVA are similar, and PVA is thus not easily melt-processed. In addition, the solution mixing method is commonly used by the majority of the PVA-based polymer composites, and a hot pressing manufacturing is rarely in conjunction with the manufacturing.^{18,19} Although the solution mixing method provides the PVA matrix with a good distribution of fillers, it also imposes restrictions on manufacturing.^{20,21} This study uses commercially available plasticized PVA²² that has a lower melting temperature and a low crystallinity, to broaden the applications of PVA-based composites.^{23–28} Therefore, this study uses the solution mixing method to prepare PVA/MWCNTs films, and several films are laminated and hot pressed to form PVA/MWCNTs composites. The control group is PVA/MWCNTs composites that are made by using the melt compounding method. This study aims to develop the combinations of the solution mixing method/hot pressing as well as the melt compounding method/hot pressing to evenly distribute the fillers in the matrices to yield greater properties and a good formation of the composites. In addition, the motivation of this study also includes proposing an efficient, eco-friendly manufacturing. These two methods are compared in terms of the properties of PVA/MWCNTs composites, which also give more variety to manufacturing. Based on our previous experience, the hot

pressing step forms a firmly molded solid when used in the final step. This then aids in the formation of the composites. The influences of solution mixing method and the melt compounding method on the tensile properties, dispersion, melting and crystallization behaviors, thermal stability, and EMI SE of the PVA/MWCNTs are then evaluated.

EXPERIMENTAL

Materials

Polyvinyl alcohol (PVA; BF-17; Chang Chun Group, Taiwan, Republic of China) has a melt flow index (MFI) of 1.67 g/3 min (160 °C/10 kg measured) and is modified by Feng Xiang Materials, Taiwan, Republic of China, by using a plasticizer.²² Multiwalled carbon nanotubes (MWCNTs; CF182C; Advanced Nanopower, Taiwan, Republic of China) have a diameter of 10–30 nm and a length of 5–20 μm .

Methods for Preparation of PVA/MWCNTs Composites

Solution Mixing Method. About 10 wt % PVA was stirred and heated in deionized water at 90 °C for 6 h to form a PVA solution. Next, MWCNTs (0, 0.25, 0.5, 1, 1.5, and 2 wt %) are added to the PVA solution, followed by being heated at 90 °C, and stirred for another 6 h. The PVA/MWCNTs mixtures are then processed for dispersion in an ultrasonic bath for 1 h. A specified volume of 20 mL of mixtures is then cast in glass dishes and dried in a vacuum oven at 60 °C for 12 h to yield PVA/MWCNTs composite films with a thickness of 0.2 mm. Ten layers of films are laminated in a mold measuring 150 × 150 × 0.5 mm³ and then compressed at 170 °C and under a pressure of 10 MPa by using a hot press machine (Yii Fuu Industrial, Taiwan, Republic of China) to form PVA/MWCNTs composites with a thickness of 0.5 mm. The process is graphically illustrated in Figure 1(a). The pure PVA plates serve as the control group.

Melt Compounding Method. PVA is dried in an oven at 60 °C for 12 h before use in the melt compounding method. To form PVA/MWCNTs mixtures, MWCNTs (0, 0.25, 0.5, 1, 1.5, and 2 wt %) are respectively melt-blended with PVA by using a brabender mixer (Tzung Wei Plastic Machinery, Taiwan, Republic of China) at 170 °C with a screw speed of 50 rpm for five minutes. The mixtures are dried in an oven at 60 °C for 12 h, followed by being placed in a mold measuring 150 × 150 ×

0.5 mm³ and hot-pressed at 170 °C with a pressure of 10 MPa by using a hot press machine (Yii Fuu Industrial) to form PVA/MWCNTs composites with a thickness of 0.5 mm. The whole process is graphically illustrated in Figure 1(b). The pure PVA plates serve as the control group.

Measurements

Tensile Tests. This test follows ASTM D638-10. The dumbbell-shaped samples are prepared as specified in ASTM D638 Type IV, and then tested for tensile strength by using an Instron 5566 (Instron). There are a total of five samples for each specification. The crosshead speed is 5 mm/min. The test results are presented in the form of tensile strength and its corresponding standard deviation, as well as the stress–strain curve.

Scanning Electron Microscopy. The fractured PVA/MWCNTs composites collected from the tensile test are affixed to the sample holder by using carbon paste, and then coated with a thin gold layer. A scanning electron microscope (SEM; S3000N, HITACHI, Japan) observes the morphology of the fractured surface morphology with an operating voltage of 15 kV.

Optical Microscopy. A few fractions of PVA/MWCNTs composites are placed on a glass slide. Samples are heated to melt at 200 °C and are then pressed to form films. An optical microscope (BX51, Olympus, Japan) observes the dispersion of MWCNTs in PVA/MWCNTs composites.

Differential Scanning Calorimetry. About 8–10 mg of PVA/MWCNTs is used for sampling, which is sealed in an aluminum sample pan, and is then placed in the differential scanning calorimeter (DSC) (Q200, TA Instruments). Samples are heated from 40 to 200 °C at 10 °C/min increments and are isothermally kept at 200 °C for 5 min to delete the thermal history. Next, samples are cooled to 40 °C with the same increments. During the second cycle, the samples are heated and then cooled between these two temperatures with the same increments, and the melting and cooling curve is recorded for the second time. The enthalpy corresponding to the melting of 100% crystalline PVA is 138.6 J/g.^{29,30} The crystallinity of PVA/MWCNTs is calculated from eq. (1).

$$X_c \% = \frac{\Delta H_m}{\Delta H_m^0 \times \varnothing} \times 100\%, \quad (1)$$

where X_c is crystallinity, ΔH_m is the apparent enthalpy of crystallization, ΔH_m^0 is the enthalpy corresponding to the melting of 100% crystalline PVA, and \varnothing is the weight fraction of PVA in the PVA/MWCNTs composites.

Thermal Gravimetric Analysis. About 8–10 mg of PVA/MWCNTs composites is placed in a ceramic sample pans and then placed in the thermal gravimetric analyzer (TGA) (TGA2950, TA Instruments). The test initials with Nitrogen (N₂) being infused, and the TGA is heated from 40 to 700 °C with increments of 10 °C/min. The thermogravimetric curve of PVA/MWCNTs composites is recorded with their initial degradation temperature being computed.

Electrical Conductivity. This test follows ASTM D4496-13 and a four-pin probe (KeithLink Technology, Taiwan) measures the electrical conductivity of PVA/MWCNTs composites. The size of

the samples is 20 × 20 × 0.5 mm³. The probe pin has a diameter of 0.08 mm, whereas the inter-pin spacing is 1.6 mm. The electrical conductivity of the composites is measured after five stabilized readings are simultaneously obtained while in contact with the 4-pin probe. In addition, samples with an electrical conductivity below 10⁻⁷ S/cm are further measured with a high resistance meter (RT-100, OHM-STAT, Static Solutions). The values that are yielded from the test are the resistivity (ρ). The electrical conductivity equation is listed as follows:

$$\sigma (\text{S/cm}) = 1/\rho = H/(R \times L \times W), \quad (2)$$

where R is the resistivity, H is the height, L is the length, and W is the width of the composites.

Electromagnetic Interference Shielding Effectiveness. An EMI shielding analyzer (EMI SE; E-Instrument Tech, Taiwan, Republic of China) measures the EMI SE of PVA/MWCNTs composites, as specified in ASTM D4935-10. Samples measuring 150 × 150 × 0.5 mm³ are placed in the coaxial transmission clamps (EM-2107A, Electro-Metrics). The spectrum analyser (Advantest R-3132, Burgeon Instrument, Taiwan, Republic of China) is equipped with an electromagnetic waves generator and then measures the samples in a scan frequency ranging between 300 kHz and 3 GHz. EMI SE is calculated by applying eq. (3),^{31,32} and is represented in decibel (dB).

$$\text{SE} = 10 \log \left[\frac{P_{\text{in}}}{P_{\text{out}}} \right] = 20 \log \left[\frac{E_{\text{in}}}{E_{\text{out}}} \right] = 20 \log \left[\frac{H_{\text{in}}}{H_{\text{out}}} \right], \quad (3)$$

where P_{in} is the incident energy, E_{in} is the electric intensity, H_{in} is the magnetic intensity, P_{out} is the transmitted energy, E_{out} is the electric intensity, and H_{out} is the magnetic intensity.

RESULTS AND DISCUSSION

Tensile Property of PVA/MWCNTs Composites

The tensile stress–strain curve of PVA/MWCNTs composites is indicated in Figure 2. Regardless of being produced by the solution mixing method or the melt compounding method, the tensile strength of PVA/MWCNTs composites increases with the increase in the MWCNTs content. This result is in conformity with the results in Figure 3. In addition, the strain of PVA/MWCNTs composites decreases with the increase in MWCNTs content, as indicated in Figure 2. Because MWCNTs are fillers with a high aspect ratio, the incorporation of MWCNTs with PVA matrix restricts the movement of PVA polymer chains. Crystallinity is another influential factor in the tensile strength of PVA/MWCNTs composites. Table I indicates that the combination of MWCNTs causes the crystallinity of the composites to increase. The MWCNTs leads to the crystallization of PVA as a result of hot pressing. The crystals of PVA can mechanically improve the composites in terms of tensile strength.³³ When applying the melt compounding method, the molecular chains of PVA are entangled as a result of the shear force caused by the brabender. The PVA/MWCNTs composites thus have an integrated and continuous structure, which results in a high strain. In contrast, applying the solution mixing method does not affect the entanglement level of PVA's molecular chains. The composites are thus not continuously constructed, and are only laminates bonded by thermal compression. The bonding

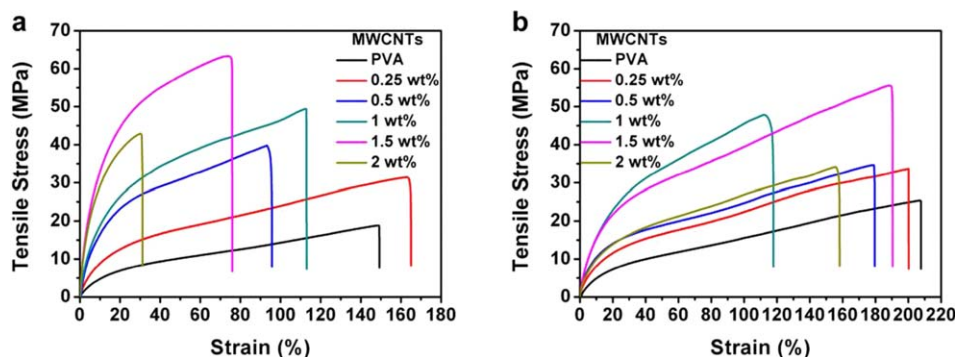


Figure 2. Tensile stress and strain curve of PVA/MWCNTs composites that are made by using (a) the solution mixing method and (b) the melt compounding method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

between laminates results in a lower ductility, which in turn causes a lower strain at break.

Figure 3 illustrates the tensile property of PVA/MWCNT composites prepared by the solution mixing method and the melt compounding method. PVA/MWCNTs composites that contain 1.5 wt % of MWCNTs have a tensile strength of 51.1 and 46.4 MPa, with their corresponding secant modulus being 264.0 and 124 MPa, respectively. The combination of MWCNTs significantly enhances the tensile strength of the composites. However, the tensile strength starts declining when MWCNTs exceeds 1.5 wt %. MWCNTs have a great aspect ratio that easily induces van der Waals force. When a great amount of MWCNTs are added, they are attracted by the van der Waals force and are thus entangled into bundles and formed a MWCNTs network. MWCNTs thus become stress concentrations. In particular, 2 wt % MWCNTs thus prevent mobility of PVA molecular chains, which has a negative influence on the tensile strength of the composites. Furthermore, the combination of MWCNTs also possibly limits the mobility and deformation of molecular chains and thereby improves the modulus of polymers. The solution mixing method provides PVA/MWCNTs composites with a greater tensile strength than the melt compounding method, because it leads to a more homogeneous of MWCNTs in PVA. This dispersion facilitates the transmission of an externally applied force. Another reason is that the PVA/MWCNTs composite membranes that are made by using the solution casting method allows for a cast directional manufacturing. The

PVA molecular chains and MWCNTs are also arranged along this direction. Therefore, after lamination and hot pressing, the PVA/MWCNTs composites are also parallel mechanically reinforced as a result of this manufacturing. The adhesion between layers is conducive for the load transmission and provides the composites with a higher tensile strength.

The PVA that this study uses is modified by using a plasticizer and thus causes a higher deformation than that of other studies.^{15,34–36} In addition, combining 1.5 wt % MWCNTs provides PVA/MWCNTs composites with a strain that is beyond 80%, which suggests that PVA/MWCNTs composites have a greater ductility.

Cross Section Morphology of PVA/MWCNTs Composites and Dispersion of Fillers

The SEM images of cross section of PVA/MWCNTs composites are indicated in Figure 4(a). Regardless of the methods, when the MWCNTs content increases from 0.25 to 2 wt %, the composites exhibit torn matrices and ductile fractures. In general, when combined with rigid fillers, most polymers indicate brittle breakage as a result of being extended by a tensile force.^{37–39} The plasticized PVA used in this study has been modified by a plasticizer and has a low crystallinity, and thus has a higher ductility. This indicates that PVA/MWCNTs composites are able to withstand greater energy and deformation, which benefits increasing the ductility of PVA/MWCNTs composites.

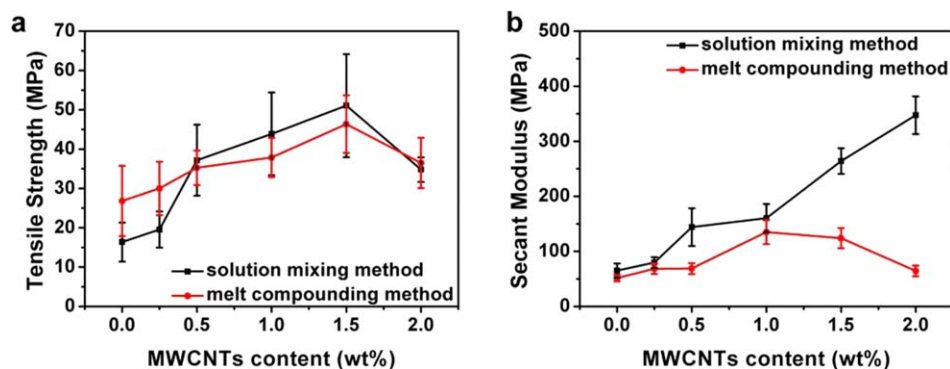


Figure 3. (a) Tensile strength and (b) secant modulus of PVA/MWCNTs composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. DSC Data of the Second Melting Curve and the Second Cooling Curve for PVA/MWCNTs Composites

MWCNTs content (wt %)	Solution mixing method					Melt compounding method				
	ΔH_m (J/g)	T_g (°C)	T_m (°C)	T_c (°C)	X_c (%)	ΔH_m (J/g)	T_g (°C)	T_m (°C)	T_c (°C)	X_c (%)
PVA	11.5	92.1	170.8	95.0	8.4	5.3	95.9	154.6	121.1	3.9
0.25	6.9	98.3	157.0	103.5	5.1	7.1	95.2	152.8	109.1	5.2
0.5	9.0	102.2	158.4	109.9	6.6	8.9	99.1	157.4	107.6	6.6
1	4.8	100.9	145.3	102.1	3.5	7.0	98.4	151.2	89.4	5.2
1.5	5.1	102.2	147.3	107.3	3.8	10.6	98.0	155.3	97.8	7.8
2	3.8	103.1	144.1	94.2	2.8	4.8	94.8	145.7	106.8	3.6

Figure 4(b) indicates the microscopic images showing the distribution of MWCNTs in the PVA matrices. When MWCNTs are increased from 0.25 to 1.5 wt %, they can be homogeneously distributed in PVA matrices. When being 2 wt %, MWCNTs easily agglomerate in PVA matrices due to van der Waals force. However, MWCNTs have a high aspect ratio and are easily entangled.^{40,41} A greater number of MWCNTs thus easily form a conductive network that contributes to a greater electrical conductivity and EMI SE.⁴²

Melting and Crystallization Behaviors of PVA/MWCNTs Composites

The PVA/MWCNT composites made by either the solution mixing method or the melt compounding method have an increasing glass transition temperature (T_g) as a result of the increasing MWCNTs, as indicated in Figure 5(a). The T_g of the pure PVA plates that are made by using the solution mixing method and the melt compounding method is 92.1 and 95.9 °C, respectively, as indicated in Table I. The T_g of the PVA/MWCNT composites containing 1.5 wt % of MWCNTs is 102.2 °C for the solution mixing method and 98.0 °C for the melt compounding method. When using the solution mixing method, and when PVA is dissolved in water, the molecular chains of the PVA are distributed in the solution. The combination of MWCNTs causes interaction between them and PVA molecular chains, which in turn decreases their mobility. It requires more energy for the mobility of the molecular chains that are restricted. Therefore, both methods increase the T_g of the PVA, which is also commonly observed in composites from previous studies.^{15,35,43}

Figure 5(b,c) and Table I show that the T_m of PVA is 170.8 °C for the solution mixing method and 154.6 °C for the melt compounding method. After 1.5 wt % of MWCNTs is added to PVA matrices, the T_m decreases to 147.3 °C (the solution mixing method) and 155.3 °C (the melt compounding method). In addition, the T_c of PVA is 95.0 °C for the solution mixing method, and 121.1 °C for the melt compounding method. After 1.5 wt % of MWCNTs is added to PVA matrices, the T_c increases to 107.3 °C (the solution mixing method), but decreases to 97.8 °C (the melt compounding method). The explanations are that the solution mixing method results in a more homogeneous status of MWCNTs, in comparison to the

melt compounding method. As a result, MWCNTs are distributed in PVA molecular chains and then affect the melting behaviors of PVA. The crystal size of PVA is decreased, and thus T_m of PVA decreases. Table I indicates that when the melt compounding method is applied, the incorporation of 1.5 wt % MWCNTs results in an increase in crystallinity of PVA/MWCNTs composites. MWCNTs serve as a nucleating agent of PVA, and thereby facilitating the crystallization of PVA during the hot pressing process. The crystallinity of PVA is thus improved as a result of the reaction between MWCNTs and PVA.³³ Bin *et al.* used 5 wt % of vapor growth carbon fiber and 5 wt % of MWCNTs in the PVA matrices, which decreased the T_m of PVA by 5 °C.⁴⁴ MWCNTs were distributed in the PVA matrices, which created greater number of nucleation sites for crystallization of PVA, and eventually increased the T_c of PVA. Ryan *et al.* added 0.5 wt % of double walled nanotubes to the PVA matrices, and the nanotubes served as the nucleation sites to induce the crystallization of PVA. The T_c of PVA increased by 13 °C.³⁶ In this study, the melt compounding method does not influence the melting behaviors of the PVA. However, it causes the poor distribution of MWCNTs in the PVA matrices, which in turn decreases the mobility of the molecular chains and, at the same time, decreases the crystallization capability of the PVA. Therefore, the T_c of composites is lower. In addition, the PVA has been modified by a plasticizer, and its hydrogen bonding is thus damaged. As a result, the stereo-regularity of the PVA's structure is decreased, and PVA has a lower melting temperature.^{24,25,27,28} The combination of MWCNTs contributes to nucleation, but also hinders the crystallization of PVA matrices, which altogether influences the melting behavior and crystallization behavior of the PVA.

Thermal Stability of PVA/MWCNTs Composites

Figure 6 shows the TGA curve and initial decomposition temperature of PVA/MWCNTs composites that are made by using the solution mixing method and the melt compounding method. Regardless of the methods, the thermal stability of PVA/MWCNTs composites is higher, in comparison to that of pure PVA matrices, as indicated in Figure 6(a). In addition, the initial decomposition temperature of PVA is 222 °C. When combining them with MWCNTs by using the solution mixing method, the initial decomposition temperature changes with

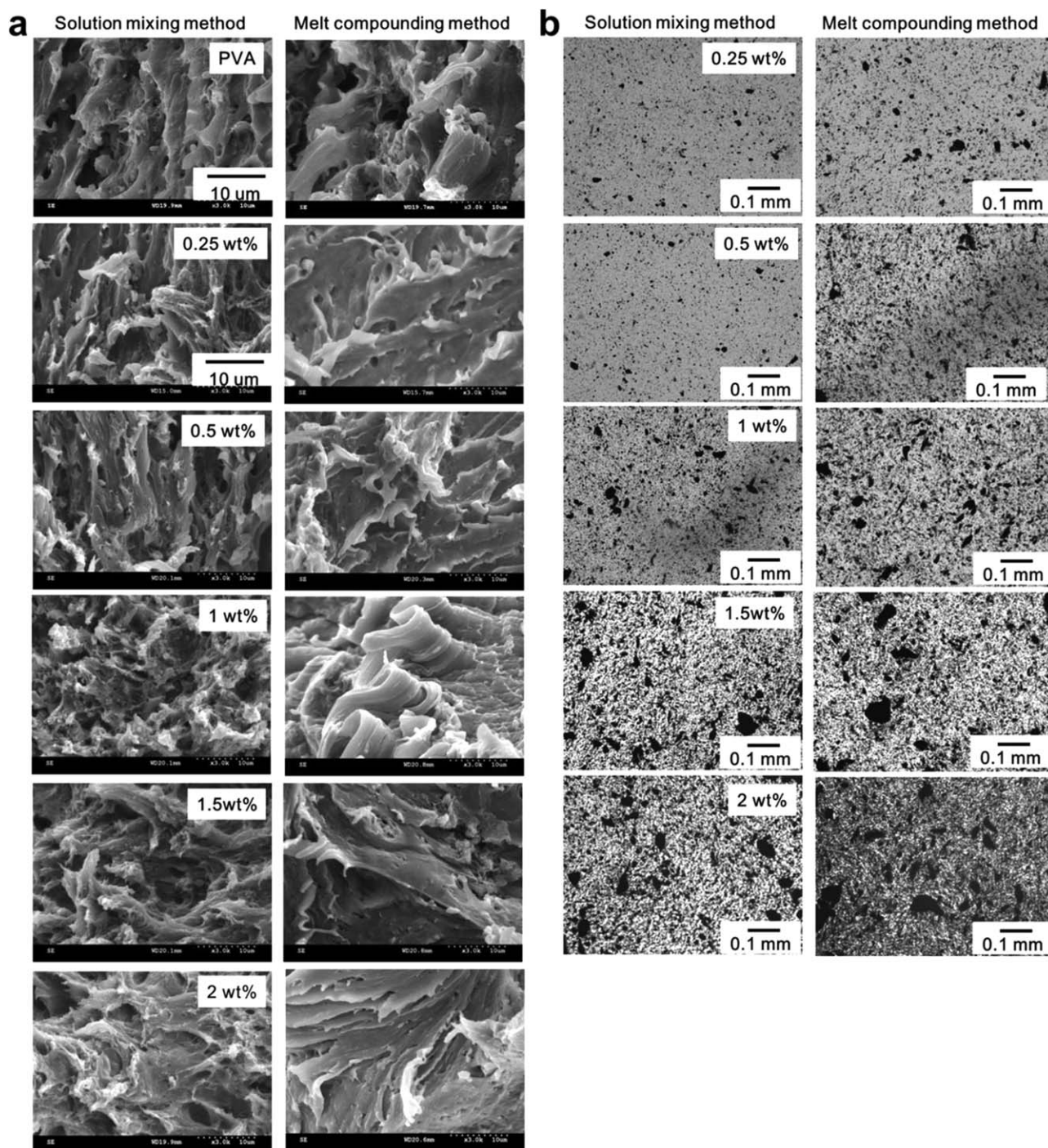


Figure 4. (a) SEM images (3000 \times) and (b) optical microscopic images (100 \times) of composites containing 0, 0.25, 0.5, 1, 1.5, and 2 wt % of MWCNTs.

different MWCNTs contents as 223 °C (0.25 wt %), 252 °C (0.5 wt %), 232 °C (1 wt %), 240 °C (1.5 wt %), and 227 °C (2 wt %). When combining them with MWCNTs by using the melt compounding method, the initial decomposition temperature changes with different MWCNTs contents as 217 °C (0.25 wt %), 229 °C (0.5 wt %), 207 °C (1 wt %), 224 °C (1.5 wt %), and 223 °C (2 wt %). In sum, the thermal stability of PVA is improved as a result of increasing MWCNTs content, as indi-

cated in Figure 6. MWCNTs are composed of carbon and thus have a good thermal stability. In comparison to the melt compounding method, the solution mixing method enables the fillers to be easily dispersed and forms a MWCNTs network in PVA matrices, which leads to the fact that the MWCNT network interacts with PVA matrix on a greater scale. As a result, PVA/MWCNTs composites made by such a method have a greater thermal stability.^{15,45}

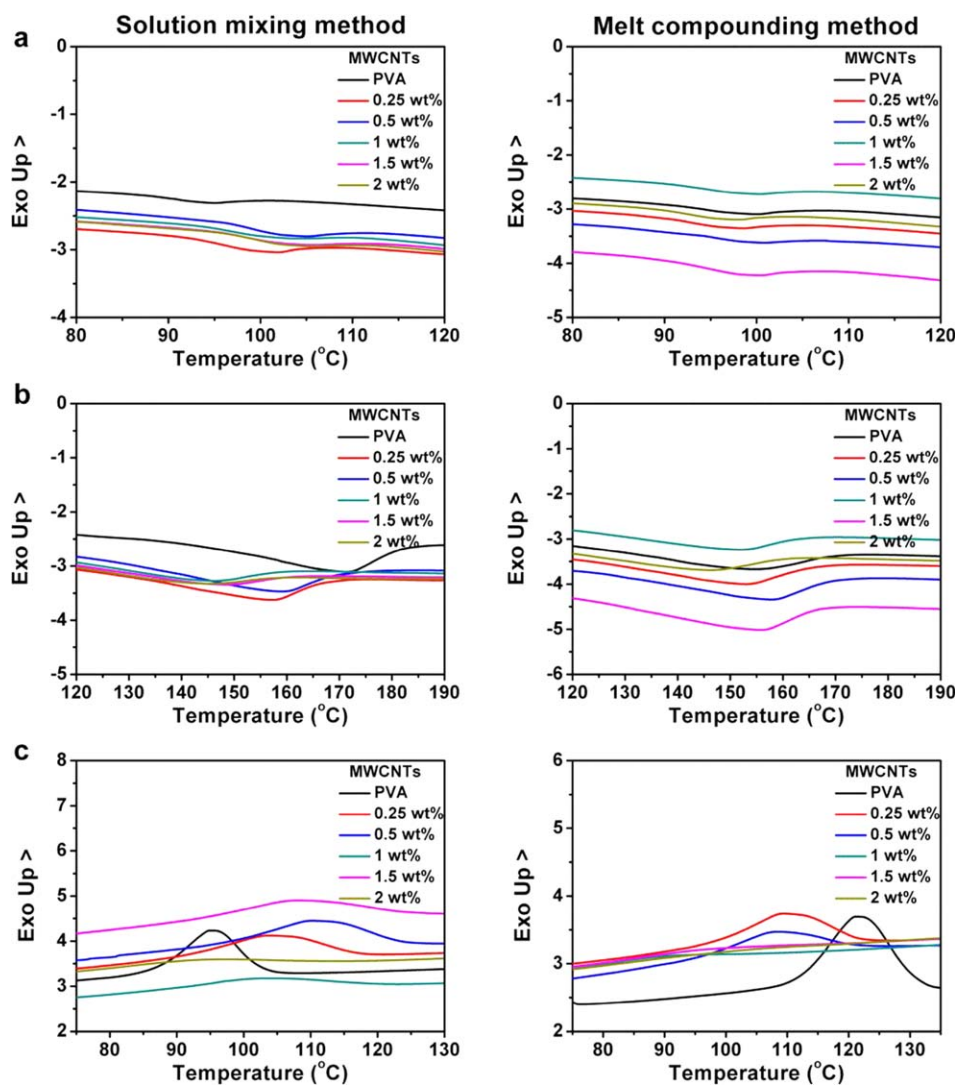


Figure 5. DSC curves of (a) glass transition temperature, (b) melting behavior, and (c) crystallization behavior of PVA/MWCNTs composites, as related to different methods. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Electrical Properties of PVA/MWCNTs Composites

The electrical conductivity of polymer composites depends on the properties, dispersion, and the formation of conductive pathways or networks of their fillers. PVA is an insulating polymer with a conductivity of 12×10^{-12} S/cm, as indicated in Figure 7. The PVA/MWCNTs composites containing 0.5 wt % of MWCNTs have a conductivity of 1.4×10^{-6} and 9.5×10^{-7} S/cm when they are made by applying the solution mixing method and the melt compounding method, respectively. This indicates that the conductivity of PVA/MWCNTs composites significantly increases by 6 and 5 orders of magnitude, in comparison to that of pure PVA matrices. In addition, the conductivity of the composites is 2.4 S/cm (the solution mixing method) and 1.4×10^{-6} S/cm (the melt compounding method). The administration of the solution mixing method can result in greater electrical conductivity and a greater EMI SE than the melt compounding method. This result is ascribed

to the even distribution of the MWCNTs in the PVA matrices, as indicated in Figure 4. Therefore, MWCNTs are evenly dispersed and then form a conductive network that provides the composites with greater electrical conductivity and EMI SE.

The EMI SE of polymer composites pertains to their electrical conductivity. In general, highly conductive materials also have high EMI SE, and as electrically conductive materials can absorb the energy brought by electromagnetic waves via consuming them as heat energy dissipation.^{46,47} EMI SE results show that regardless of the methods, PVA/MWCNTs composites barely exhibit EMI SE when comprising a small content of MWCNTs, as indicated in Figure 8. In comparison to Figure 8(a,b), the EMI SE of the composites increases with the increasing content of MWCNTs. The majority of the MWCNTs is connected to form a continuously conductive network, and thereby transforms the insulating polymer into a semiconductor or a conductor. The PVA/MWCNTs composites are electrically conductive,^{43,48} and simultaneously possess EMI SE.

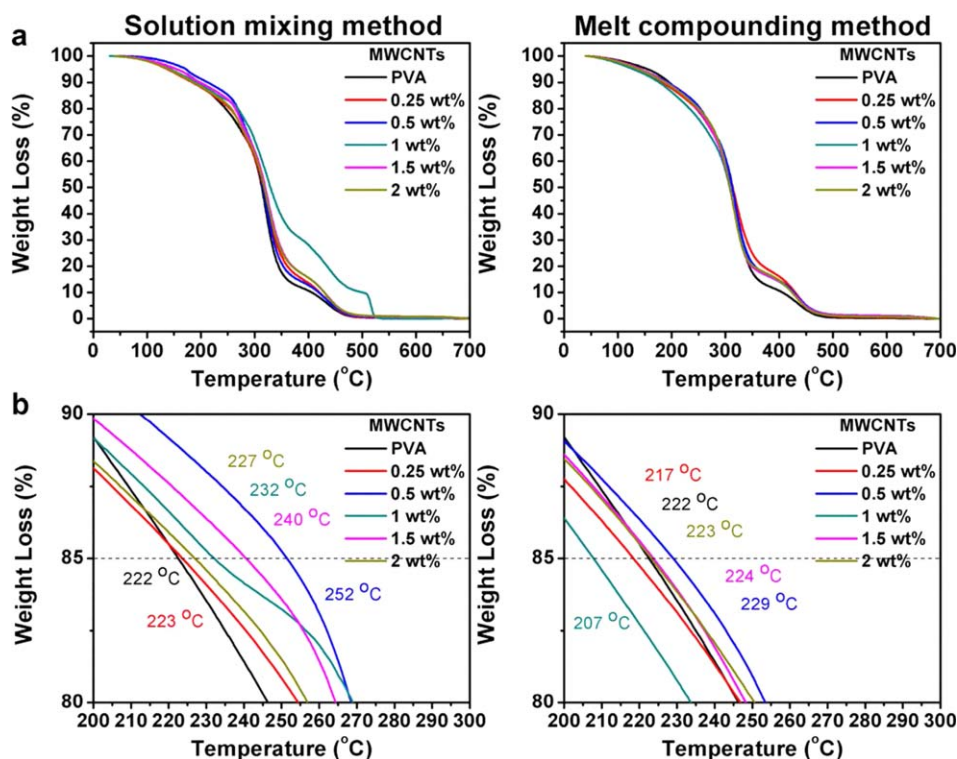


Figure 6. (a) TGA curve and (b) initial decomposition temperature of the thermal stability of PVA/MWCNTs composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

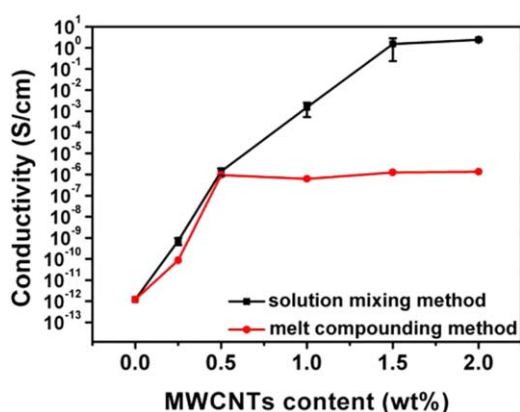


Figure 7. Electrical conductivity of PVA/MWCNTs composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

By applying the solution mixing method, PVA/MWCNTs composites consisting of 2 wt % of MWCNTs have an average EMI SE of -30.74 dB, which is qualified for the EMI SE standard required by livelihood necessities. Daily electronic and electron equipment often has a radio spectrum of 1–3 GHz, and PVA/MWCNTs composites also have their optimal EMI SE of -31.41 dB in this frequency range, which is surmised to be due to intrinsic properties of their fillers, as summarized in Table II. Such results may be ascribed to the intrinsic properties of the fillers.^{49,50} In contrast, PVA/MWCNTs composites that are made by applying the melt compounding method do not exhibit EMI SE, and furthermore, their electrical conductivity is evaluated to be more suitable for electrostatic dissipative protection materials.⁵¹

Moreover, the administration of the solution mixing method can result in a greater electrical conductivity and a greater EMI SE than the melt compounding method. In comparison to the

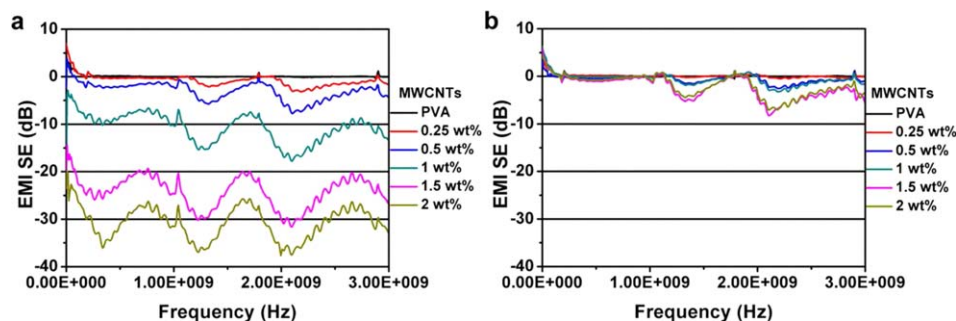


Figure 8. EMI SE of PVA/MWCNTs composites that are made by applying (a) the solution mixing method and (b) the melt compounding method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. EMI SE Data of PVA/MWCNTs Composites

MWCNTs content (wt %)	Solution mixing method			Melt compounding method		
	EMI SE(dB) (0.0003–1 GHz)	EMI SE(dB) (1–2 GHz)	EMI SE(dB) (2–3 GHz)	EMI SE(dB) (0.0003–1 GHz)	EMI SE(dB) (1–2 GHz)	EMI SE(dB) (2–3 GHz)
PVA	0.31	−0.04	−0.02	0.31	−0.04	−0.02
0.25	0.16	−0.78	−1.76	0.36	0.06	−0.12
0.5	−1.51	−2.98	−4.57	−0.13	−0.31	−1.24
1	−8.06	−11.33	−12.75	0.30	−0.42	−1.59
1.5	−22.24	−25.13	−25.19	−0.27	−1.95	−4.67
2	−29.40	−31.42	−31.41	−0.11	−1.58	−4.15

dispersion of the fillers that is shown in Figure 4, it can be concluded that the EMI SE is correlated with the conductivity as well as the content and dispersion of the conductive fillers.

CONCLUSIONS

This study has shown that the solution mixing method is more suitable under these experimental conditions to synthesize composites that have greater tensile properties, dispersion, thermal stability, electrical conductivity, and EMI SE in relation to PVA/MWCNTs composites. The test results indicate that the solution mixing method allows for a better dispersion of MWCNTs in the PVA matrices, and the PVA/MWCNTs composites thus have greater properties. The tensile strength of PVA/MWCNTs composites that are composed of 1.5 wt % of MWCNTs is 218% greater than that of pure PVA matrices. Regardless of the amount of MWCNTs, all of the composites have greater thermal properties. In addition, the electrical conductivity and EMI SE of the PVA/MWCNTs composites containing 2 wt % of MWCNTs are 2.4 S/cm and −30.74 dB for the solution mixing method, as well as 1.4×10^{-6} S/cm and −1.95 dB for the melt compounding method. Therefore, this study provides a manufacturing procedure that can reinforce polymer composites, which applies the solution mixing method to distribute fillers in PVA and then applies hot pressing to form the PVA-based composites. The manufacturing procedure contributes a good dispersion of fillers and an eco-friendly process, and therefore, this study creates PVA/MWCNTs composites via the solution mixing method, which reaches the EMI SE grade of civil necessities, and desired mechanical and thermal properties. Thus, they are expected to be applied to packaging materials for home appliance and spare parts of electrical optical instruments.

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