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Research article

Synthesis and characterization of surface modified MWCNTs reinforced PVA composite films

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ABSTRACT

Polymers have been ruling the packaging industry for decades due to their versatility, easy manufacturability, and low cost. The overuse of non-biodegradable plastics in food packaging has become a serious environmental concern. Multi-walled carbon nanotube (MWCNT) reinforced nanocomposites have exceptional electrical, thermal, and mechanical properties. However, a major difficulty in the synthesis of CNT-reinforced nanocomposites is the nanotube agglomeration, which results in poor dispersion and less interfacial bonding between reinforcements and matrix, limiting its advantages. Although acid treatment is effective, strong acids, treatment timing, and sonication power can lead to nanotube damage. This study introduces a novel approach to enhance PVA nanocomposite films' mechanical, thermal, optical, and antibacterial performance using polydopamine-coated CNTs, which are more effective than pristine or acid-treated CNTs, making them promising for food packaging applications. Pristine CNT reinforced polyvinyl alcohol (PVA) nanocomposite films were fabricated with varying concentrations of CNTs (0 wt%, 0.5 wt%, 1.0 wt%, 1.5 wt%, and 2.0 wt%). These samples underwent mechanical, thermal, and optical characterization for the optimization of CNTs' concentration in the PVA matrix. Then the optimized amount of acid-treated and polydopamine-coated CNTs was used to fabricate PVA/CNT films. The mechanical, thermal, and optical characteristics of the resultant films were investigated. It was found that the polydopamine coating on CNTs improved the mechanical, thermal, and optical properties of the films as compared to those of pure PVA, PVA/pristine CNT, and PVA/acid-treated CNT films. Moreover, the resultant film also demonstrated good antibacterial activity against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) in comparison to pure PVA.

1. Introduction

Widely used polymers in food packaging applications include polyethylene (PE), polystyrene (PS), polypropylene (PP), polyvinyl chloride (PVC) and polyethylene terephthalate (PET) [1]. Although these materials have been fulfilling the packaging needs properly, their disposal has become a momentous issue due to their slower degradation as well as difficulty in removal of their smaller pieces

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from contaminated water [2,3]. In addition, they pose serious risks to human health through primary, secondary, and incidental ingestion [4], skin diseases, eye irritation, respiratory problems, cancers, liver dysfunction, reproductive problems, and cardiovascular diseases [5].

Although the eco-friendliness of biomaterials is much appreciated, poor mechanical properties and material processing abilities limit their applications in food packaging. Polyvinyl alcohol (PVA) is a well-known, widely available, non-toxic, inexpensive, water soluble, biodegradable synthetic biopolymer with moderate mechanical strength, excellent film forming ability, resistance to chemicals, oil, and grease, and high crystallinity. Therefore, it has been used in medicine cachets, controlled drug delivery systems, surgical yarns, and packaging, for years [6]. Further improvement of the properties of PVA can be done by reinforcement of filler materials in the matrix. To increase the matrix-filler interaction, size reduction of filler has been found to be effective owing to the high surface area to volume ratio, which leads to nanotechnology [7]. The addition of nanomaterials like CNTs is found to increase the mechanical strength, barrier property, thermal stability, antimicrobial activity, and bio-sensing properties of the nanocomposites well suited for food packaging [8,9,10]. Many bacteria have been found to be exterminated by means of direct interaction with CNTs, probably due to the long and thin CNTs' penetration into the microbial cells, inflicting irreparable damage [11,12]. The property improvement greatly depends on the geometry, mechanical property, interfacial property, loading level, and dispersion ability of the nanoparticles [13]. The key challenges in fabricating polymer matrix composites by reinforcing CNTs are to ensure homogenous CNT dispersion within the matrix and to attain solid interfacial adhesion of CNTs with the matrix [14]. So, to reduce agglomeration, promote dispersion, increase polymer-CNT interfacial bonding, and reduce toxicity, purification, and functionalization of CNTs are necessary. Because of its adaptability, effectiveness, and scalability, acid treatment is widely used to enhance the characteristics of CNTs by generating carboxylic groups on their surfaces, increasing their dispersibility [15,16,17]. Although acidic functionalization of CNT is effective but strong acid, treatment timing and sonication power can lead to the incorporation of defects on the graphitic network and fragmentation of nanotubes [18,19].

Polydopamine deposition by oxidative polymerization of dopamine is becoming more popular as a bio-inspired surface modification approach. Dopamine (2-(3,4-dihydroxyphenyl) ethylamine) is a hormone and neuromodulator molecule found in a wide range of animals and plants. Oxidization of neutral dopamine forms dopaminochrome, which eventually transforms into polydopamine by oxidative polymerization and creates a hydrophilic coating that can protect against oxidizing agents and pathogens [20]. CNTs can be coated with polydopamine without affecting the nanotube sidewalls to have hydrophobicity with improved water dispersibility and increased biocompatibility by reducing the cytotoxicity of nanomaterials [21,22,23]. Moreover, the use of biomolecules to functionalize CNTs can reduce toxicity [24].

Despite having potential as a promising material due to its exceptional properties, very few research has been reported to investigate CNTs' application in food packaging. A review of different experimental studies clearly showed the pristine CNTs' limitations and the effect of acidic treatment timing, sonicating timing and power, and acid concentration on the nanotubes. Although surface modification of CNTs is known to enhance their dispersion and compatibility with polymer matrices, the effect of biopolymer functionalization techniques on the properties of polymer-based CNT nanocomposite films remains unclear. Moreover, the investigation of the compatibility between PVA and biopolymer modified CNTs is still ambiguous. This study focuses on generating a novel approach to observe the impact of biopolymer functionalization techniques on the characteristics of PVA/CNT nanocomposite films. In this study, MWCNTs have been treated with acid and polydopamine. PVA/pristine CNT nanocomposite films were fabricated with different amounts of MWCNTs viz. 0 wt%, 0.5 wt%, 1.0 wt%, 1.5 wt%, and 2.0 wt%. Mechanical, thermal, optical, and antibacterial properties of the resultant composite films were investigated for their possible use in food packaging.

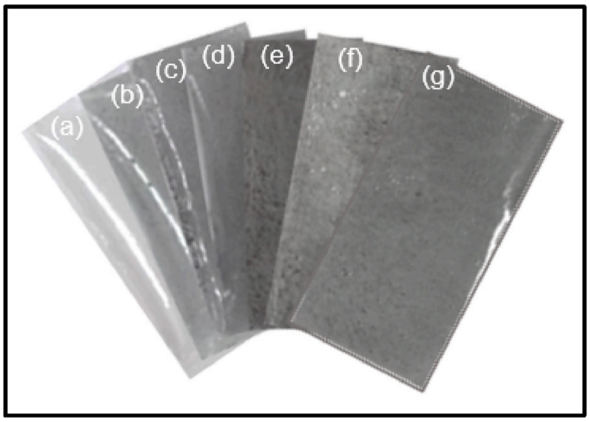


Fig. 1. PVA/CNT films a) PVA/0 CNT, b) PVA/0.5 CNT, c) PVA/1.0 CNT, d) PVA/1.5 CNT, and e) PVA/2.0 CNT, f) PVA/2.0 CNT-Ac, and g) PVA/2.0 CNT-Pd.

2. Materials and methods

2.1. Materials

Multi-walled carbon nanotubes (MWCNT-SE-001, Research grade, diameter 5–20 nm, purity 99 %, length 10 μm) were purchased from SHILPENT Enterprise, Nagpur, India and PVA powder was purchased from Loba Chemie. H_2SO_4 (Merck, 98 %), HNO_3 (Merck 65 %), HCl (Merck, 37 %), dopamine (melting point 243–250 °C), and tris (melting Point 175 °C) were purchased from Modern Scientific Co. Ltd., Dhaka.

2.2. Functionalization of MWCNTs

2.2.1. CNT acid treatment

Pristine CNTs were acid treated using a 3:1 solution of HCl and deionized (DI) water. 100 mg of CNTs were added to 30 ml HCl and 10 ml DI water solution. After magnetic stirring at room temperature for 1 h at 400 rpm, CNTs were separated by centrifugation and washed with DI water until neutralized. CNTs were then dried overnight at 100 °C, and this sample was marked CNT-H. Later, these CNTs were further acid treated using 3:1 solution of H_2SO_4 and HNO_3. 50 mg of CNT-H were added to 30 ml H_2SO_4 and 10 ml HNO_3 solution. After magnetic stirring at room temperature for 4 h at 400 rpm, CNTs were separated similarly by centrifugation and washing. Acid treated CNTs were then dried in a hot air oven at 100 °C overnight, and this sample was marked as CNT-Ac (Fig. 1(f)).

2.2.2. Polydopamine coating on CNT surface

50 mg of pristine CNTs, 100 mg of dopamine, and 60 mg of tris were added to 50 ml of DI water. The suspension underwent sonication for 1 min and magnetic stirring at room temperature for 24 h at 400 rpm. Separation of CNTs was done by centrifugation and washing with DI water until neutralized. These coated CNTs were then dried in a hot air oven at 100 °C overnight, and this sample was marked as CNT-Pd (Fig. 1(g)).

2.2.3. Fabrication of composite films

4 wt% of PVA solution was heated with magnetic stirring at 300 rpm for 1 h at 85 °C. Pristine CNTs of different concentrations viz. 0 wt% (Fig. 1(a)), 0.5 wt% (Fig. 1(b)), 1 wt% (Fig. 1(c)), 1.5 wt% (Fig. 1(d)), and 2 wt% (Fig. 1(e)) were then added to this solution with continued stirring and heating for another 1 h. Later, for better dispersion, the suspension was kept in ultrasonic bath for 10 min and then, was poured into the mould and dried at 100 °C overnight in a hot air oven to obtain the films. The same procedure was followed to fabricate all the CNT reinforced PVA films. The obtained films are shown in Fig. 1.

2.2.4. Characterization

Tensile test was conducted using a micro-computer controlled electromechanical universal testing machine (model: ETM 502A) following ASTM D638-2003 at room temperature. For each specification, five samples were tested by continuously recording applied force and associated strain using crosshead velocity of 5 mm/min. Differential scanning calorimeter (DSC) (model: DSC131 EVO) was used to obtain DSC thermographs at a heating rate of 10 °C/min between 25 and 600 °C temperature. Thermal gravimetric analyzer (TGA) was used to study the decomposition behavior of the films at a heating rate of 10 °C/min between 25 and 600 °C temperature. Absorbance of pure PVA, PVA/pristine CNT, and PVA/treated CNT films was measured using a LAMBDA 365 UV–vis spectrophotometer for wavelength range of 200–1100 nm at room temperature.

Field emission scanning electron microscopy (FE SEM) (model: JSM 7600F, JEOL-Japan) was used to observe the surface morphology of pristine and surface modified CNTs. Accelerating voltage was 10 kV, probe current was 1.00 nA, PHA mode was T3, and energy range was 0–20 keV. To confirm surface modification of CNTs with acid and coating with polydopamine, Fourier-transform infrared (FTIR) spectra of pristine CNTs, CNT-Ac and CNT-Pd were recorded using IRAffinity-1S in the wavenumber range of 500–4000 cm^{-1}.

By using the colony counting method, antibacterial test was conducted against gram-positive *Staphylococcus aureus* (RM_AST_SA012) and gram-negative *Escherichia coli* (DH5x) bacteria to evaluate the antibacterial activity of PVA and PVA/2.0 CNT-Pd films. In this procedure, a single colony of bacteria was cultured overnight in nutrient broth at 37 °C. Following that, in 15 mL of the diluted broth, the samples were incubated at 37 °C and later, diluted in sterile saline for the desired duration of time. Then, bacterial solutions with and without samples were plated in individual agar plates with proper time labeling and stored in an incubator for observation. Bacterial colonies from each period were combined after 18–24 h to determine if bacterial colonies had been resurrected or killed. A fresh plate of bacterial solution without any sample was used to monitor the normal bacterial growth under the same circumstances. Eqn. (1) was used to determine the proportion of bacteria that were killed at the specified period:

$$\text{Bacteria killed (\%)} = [(N_0 - N_t) / N_0] \times 100 \qquad \text{Eqn. (1)}$$

Where N_0 = number of surviving bacteria and N_t = number of bacteria at a specified time in the sample.

3. Results and discussion

3.1. Mechanical properties of PVA/pristine CNT composite films

Fig. 2(a) represents the stress-strain curves of PVA/pristine CNT composites with different content of CNTs viz. 0 wt%, 0.5 wt%, 1.0 wt%, 1.5 wt%, and 2.0 wt% where incorporation of CNTs increased tensile strength by 14 %, 28 %, 90 %, and 111 %, respectively (Fig. 2(b)). This can be attributed to the inhibition of PVA polymer chain mobility by means of restricted sliding or spinning on addition of CNTs, since CNTs act as fillers due to its high aspect ratio [25]. As the mobility of the polymer gets restricted, obviously the stress required to deform the material get increased. Also, due to load transfer from PVA matrix to the CNTs with exceptionally strong, rigid, and high modulus of elasticity, tensile strength was increased by dispersion strengthening mechanism [26]. The strong mechanical properties and high aspect ratio of CNTs also delay film's propensity to break by crack bridging and crack deflection mechanisms, which prevent cracks from spreading and increase overall resistance to failure [27]. In contrast, incorporation of small amount of CNTs reduced elongation of the composite since high aspect ratio of CNTs resulted in the impeded polymer chain motion (Fig. 2(c)). However, an increasing trend in elongation was noticed with further CNTs addition. Similar result was also reported by Zohora et al. for CNT reinforced chitosan/PVA composites [27,28].

3.2. Melting and crystallization behaviors of PVA/pristine CNT composite films

Fig. 3(a)-3(e) show the DSC thermographs of PVA/pristine CNT composite films where three of the main transition temperatures, i.

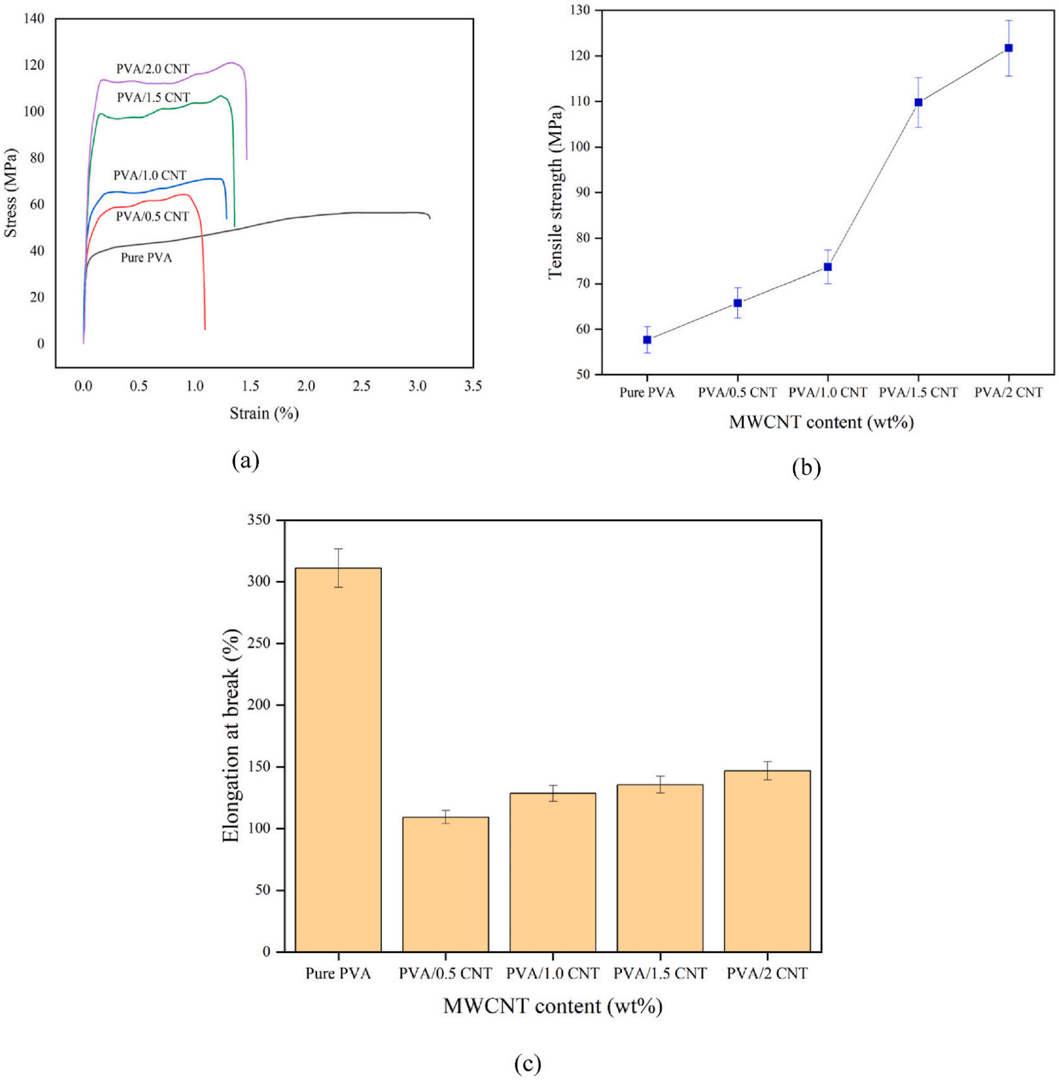


Fig. 2. (a) Stress-strain curves, (b) tensile strength, and (c) elongation at break of pure and pristine CNT reinforced PVA films.

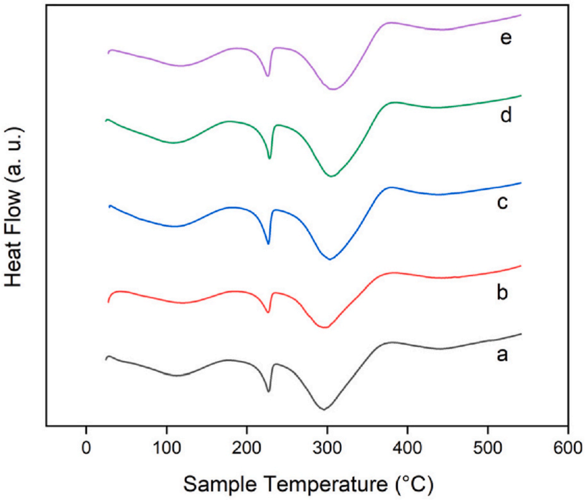


Fig. 3. DSC curves of a) pure PVA, b) PVA/0.5 CNT, c) PVA/1.0 CNT, d) PVA/1.5 CNT, and e) PVA/2.0 CNT composite films.

e., glass transition temperature (T_g), melting temperature (T_m), and crystallization temperature (T_c), were identified. A minor endothermic peak between 24 and 55 °C was observed due to the removal of water as well. The DSC data for PVA/CNT composite films are presented in Table 1. The incorporation of CNTs in PVA matrix noticeably increased the value of T_g in all the composite films. Similar results were reported in previous studies [29,30]. Due to solution mixing, well distribution of PVA molecular chains occurs after PVA hydrolysis. When CNTs are added, they interact with these molecular chains and strengthen interfacial bonding. The segmental motion of the polymer molecules is constrained by the entanglement and trapping of PVA chains between the CNTs. As the motion of the molecular chains is restricted, more energy is required for their mobility, which in turn increases T_g [31,32]. Besides, the introduction of rigid and high aspect ratio CNTs in the matrix improved the stiffness and strength of the films and increased the overall rigidity of the PVA matrix, which in turn raised T_g [33]. There may not always be a linear trend in the association between the weight percentage of CNTs and T_g. Non-linear variations in T_g can be caused by the addition of nanofillers because they can cause complicated interactions and alterations in the polymer matrix. Because of the intricate interplay between dispersion, agglomeration, and interfacial interactions, different concentration ranges could exhibit distinct effects. The highest increase in T_g was obtained when the CNT concentration approaches 2 wt%. This increase could be attributed to efficient CNT dispersion at this concentration, which improved reinforcement across the matrix and not just in localized regions. In comparison to other concentrations, T_g is higher due to the improved load transfer and reinforcement provided by the enhanced interactions and better dispersion [34]. The mobility of the polymer chains and composite's overall T_g can both be impacted by the interfacial interactions between CNTs and PVA. At 2 wt% CNTs addition, optimal dispersion conditions might exist, which could counterbalance the agglomeration effects and lead to an increased T_g.

The value of T_m reduced for most of the reinforced films. The addition of CNTs to the matrix can enhance its free volume and disrupt connections between polymer chains, which, eventually, lowers melting point [35,36]. A similar result has been reported by Bin et al., where melting temperature was reduced by using a mixture of carbon fiber and CNTs in a PVA matrix [37]. The development of intermolecular connections or physical crosslinking between CNTs and PVA matrix might be responsible for higher melting temperature observed in 1.5 wt% CNT/PVA film. The energy barrier for molecular mobility may rise because of this interaction, raising the melting point in the process.

Crystallization temperature, T_c, was also increased on CNTs addition. This is because, for the crystallization of PVA, CNTs serve as nucleating agents and provide more locations to arrange and create crystalline structures [35]. As PVA crystals are more likely to form because of their greater nucleation density, the temperature needed to start and finish the crystallization process must be higher. The CNTs and PVA chains' contact and entanglement restrict the polymer segments' motion, making it more difficult for them to

Table 1
DSC data for PVA/pristine CNT composite films.

Sample	T_g (° C)	T_m (° C)	T_c (° C)
Pure PVA	82	228	177
PVA/0.5 CNT	85	226	183
PVA/1.0 CNT	84	227	182
PVA/1.5 CNT	83	229	178
PVA/2.0 CNT	86	227	184

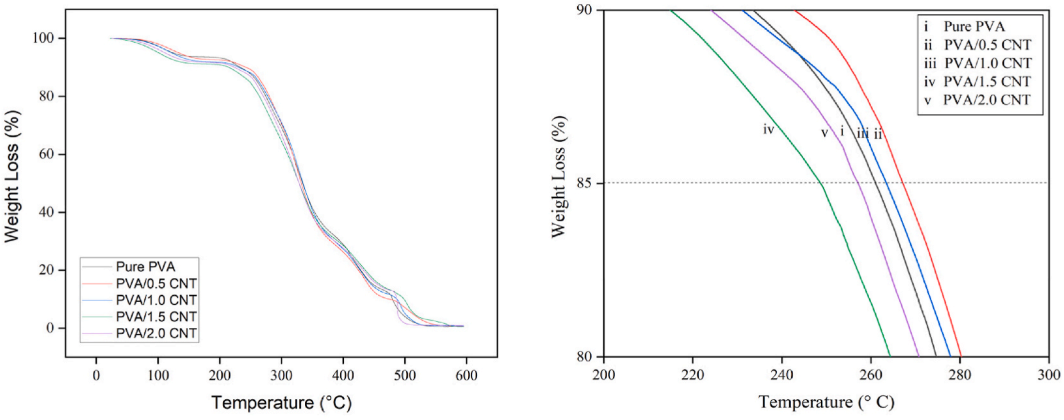
reorganize and produce crystalline areas. As a result, greater temperatures are needed to overcome this obstacle and enable crystallization. The improved interfacial interactions between the nanotubes and the PVA matrix may encourage PVA chain ordering close to the CNT surface, which will aid in crystallization. The higher energy barrier for crystallization is a result of the enhanced interfacial interactions, necessitating a higher temperature to start the process. Again, the trend of increased in T_c is non-linear as in T_g. The highest crystallization temperature is noticed for 2.0 wt% of CNTs addition, which can be explained by the higher dispersion and interaction of the CNTs with the polymer matrix. However, agglomeration or cluster formation due to less uniform CNT dispersion within the polymer matrix might impede nucleation and results in less increase in T_c in some cases. Again, too many CNTs might hinder the mobility of the polymer chains, which increase difficulty in the formation of crystalline structures.

3.3. *Thermal stability of PVA/pristine CNT composite films*

Thermal decomposition characteristics of pure PVA and PVA/CNT nanocomposite films were analyzed using TGA (Fig. 4(a)). The thermal decomposition behavior of the studied samples shows three distinct segments. The first weight loss of pure PVA occurs at temperatures between 50 and 150 °C owing to evaporation of solvent that was absorbed, decomposition of PVA is responsible for the second step, which involves a significant weight loss between 210 and 370 °C; and continued disintegration of the remainders is responsible for the third stage of weight loss between 370 and 550 °C [38]. Fig. 4(b) illustrates that from the starting decomposition temperature of pure PVA at 261 °C, the value increases for PVA/0.5 CNT and PVA/1.0 CNT films. This increase indicates the thermal steadiness of the PVA matrix after the introduction of CNTs [28,25], [25,28]. The thermal stability of the composite can be improved by a CNT network, that is tightly bound and well-dispersed, however, weak interactions or poor dispersion may have the opposite effect as observed for higher amount of CNTs addition. CNTs have a high thermal conductivity, which can enhance the composite films' ability to transmit heat. A modest rise in the initial decomposition temperature can be caused by CNTs addition because they can improve heat dissipation throughout the breakdown process. Since CNTs are thermally stable, they can resist higher temperatures without breaking down and thereby, increase the initial decomposition temperature. The thermal behavior of the composite films can also be influenced by the interaction between CNTs and PVA matrix. A strong interfacial connection can limit polymer chain mobility and impede breakdown. This may delay decomposition and reach a greater initial decomposition temperature for PVA/0.5 CNT and PVA/1.0 CNT films. However, further increase in CNT content resulted in reduced initial decomposition temperature. For some thermal reactions, such as breakdown of polymer matrix, CNTs can function as catalysts. The addition of CNTs may speed up the degrading process and lower the initial decomposition temperature of composite [39]. High thermal conductivity of CNT might impact PVA's ability to transmit heat and cause reduction of localized temperatures as well as faster heat dissipation, potentially lowering the initial decomposition temperature. CNTs' weight fraction or concentration in the composite can have an impact on thermal stability. The initial higher decomposition temperature of PVA/CNT films for 0.5 wt% and 1.0 wt% CNTs addition might be a result of the positive effect that CNTs at low concentrations have. However, the initial decomposition temperature dropped at higher concentrations (1.5 wt% and 2.0 wt%), possibly due to agglomeration or excessive CNT loading that had an adverse impact on the thermal stability.

3.4. *UV–vis spectroscopy of PVA/pristine CNT composite films*

Although just 3 % of sun's total radiation consists of UV rays, it can nevertheless cause chemical reactions, fade specific colors, breakdown polymers, and perhaps, cause damage to eyes and skin. As a result, to define the final applications, UV shielding effectiveness of polymer materials is needed to be tested. UV–vis spectroscopy was utilized to analyze the optical characteristics of PVA/pristine CNT and pure PVA/surface modified CNT films. The transmittance vs. wavelength plots of pure and PVA/pristine CNT films



(a)

(b)

Fig. 4. (a) TGA curves and (b) initial decomposition temperature of pure and pristine CNT reinforced PVA films.

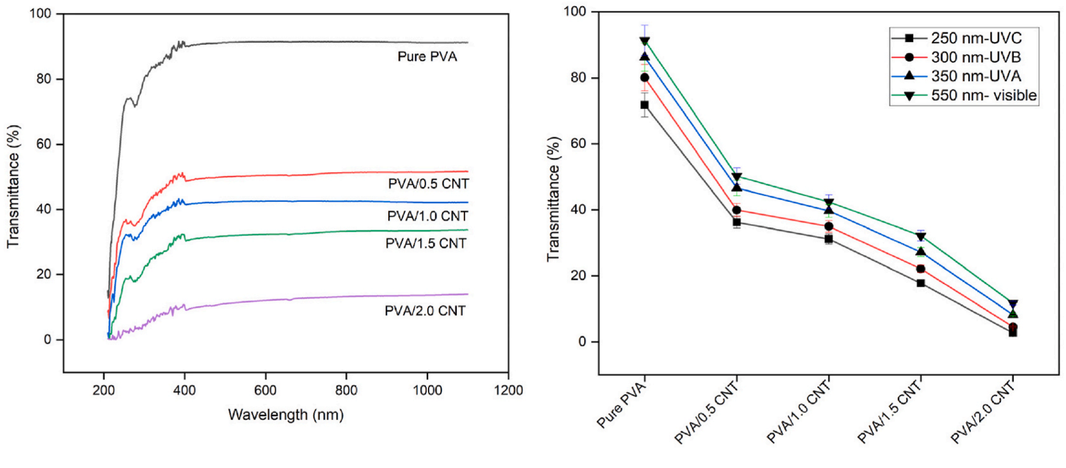
are shown in Fig. 5(a). Since the ratio of photons passing through a sample (I) and under an incident light (I_0) may be used to determine the transmittance of a sample (T), I/I_0, a transmittance of nearly 100 % indicates a film that is totally transparent to the incident light. Although PVA is colorless and transparent, with increasing percentage of CNT, the transparency gradually falls. Fig. 5(b) shows that transmittance of pure PVA film is more than 90 % across the visible spectrum (400–700 nm) and addition of CNTs to PVA results in a progressive drop in visible light transmission. The PVA/2.0 CNT film exhibits up to 12 % transmittance at 550 nm, indicating a major reduction in optical transparency compared to pure PVA. Additionally, it should be highlighted that when CNTs are added to PVA, even at a level as low as 0.5 wt%, there is a dramatic increase in UV absorption as opposed to pure PVA, which exhibits negligible absorption in the UV band from 200 to 400 nm. PVA/0.5 CNT film shows transmittance above 50 %, which means CNT nanoparticles have improved UV light shielding properties in the targeted spectrum. Koozekonan et al. also reported decrease in transmittance with increased CNT content in polyacrylonitrile matrix [40]. To assess effectiveness of UV shielding, transmittance of PVA and PVA/pristine CNT films at particular wavelengths of UV light were examined as shown in Fig. 5(b). Since PVA/pristine CNT films display good UV light absorbance at 250 nm (UVC), 300 nm (UVB), and 350 nm (UVA), they are suitable as UV-shielding materials. For example, plain PVA only blocks 13.74 % UVA, 19.97 % UVB, and 28.25 % UVC, whereas PVA/2.0 CNT film can block nearly 97.29 % UVC, 95.43 % UVB, and 91.72 % UVA. Therefore, addition of CNT to PVA can improve absorbance of UV rays and create unique materials with exceptional UV-shielding properties. UV-shielding capacity of the resulting PVA/CNT nanocomposite films is quite like that obtained using alternative organic or inorganic UV absorbent materials [41].

3.5. FE SEM

Fig. 6 (a)-6(c) represent FE SEM images of pristine and surface modified CNTs. The increased thickness and changes in surface texture of CNTs through modifications are clearly noticeable.

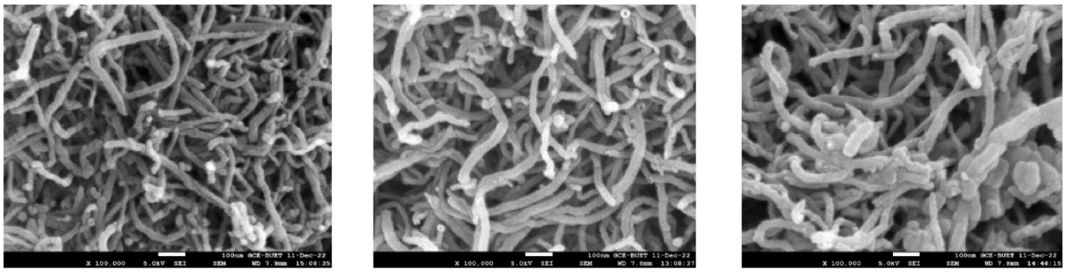
3.6. FTIR spectroscopy

To validate the existence of functional groups, FTIR spectroscopy of pristine CNT, CNT-Ac and CNT-Pd were performed as represented by Fig. 7. For pristine CNT, weak band was observed between 1580 and 1600 cm^{-1} which is induced by stretching vibrations of C-C bonds in CNT structure [42]. A new peak around 1700–1800 cm^{-1} corresponding to stretching vibrations of carboxylic acid (C=O) functional groups, arises after acid functionalization. This peak represents the appearance of carboxylic acid compounds on the surface of CNT because of acid treatment [43]. The stretching vibrations of the C-O bonds in carboxylic acid groups led to the appearance of a peak at 1240 cm^{-1}. Peaks at 3585 cm^{-1} and 1700 cm^{-1} have been seen for CNT-Pd. The peaks at 3200–3600 cm^{-1} can be attributed to O–H and N–H stretching modes because of dopamine functionalization [20]. Two hydroxyl (-OH) groups in dopamine can interact with the carboxyl groups on the surface of CNTs to create additional O-H bonds. The reaction between the aromatic amino groups of dopamine and the CNTs was indicated by the band at 1600–1750 cm^{-1}, which reflected O=C, N–H, and C=C bonding [44]. The aromatic ring, which contains the C=C (ring), C=N (ring), and C-N-C (ring) functional groups of dopamine, shows a distinctive peak at 1242 cm^{-1}. These results show that CNT surface has been successfully functionalized with dopamine.



(a) (b)

Fig. 5. (a) UV–vis spectra, and (b) change in transmittance at particular UV radiation wavelengths (UVA, UVB, and UVC) of pure and pristine CNT reinforced PVA films.



(a) (b) (c)

Fig. 6. FE SEM images (100000 ×) of (a) pristine CNT (b) CNT-Ac, and (c) CNT-Pd.

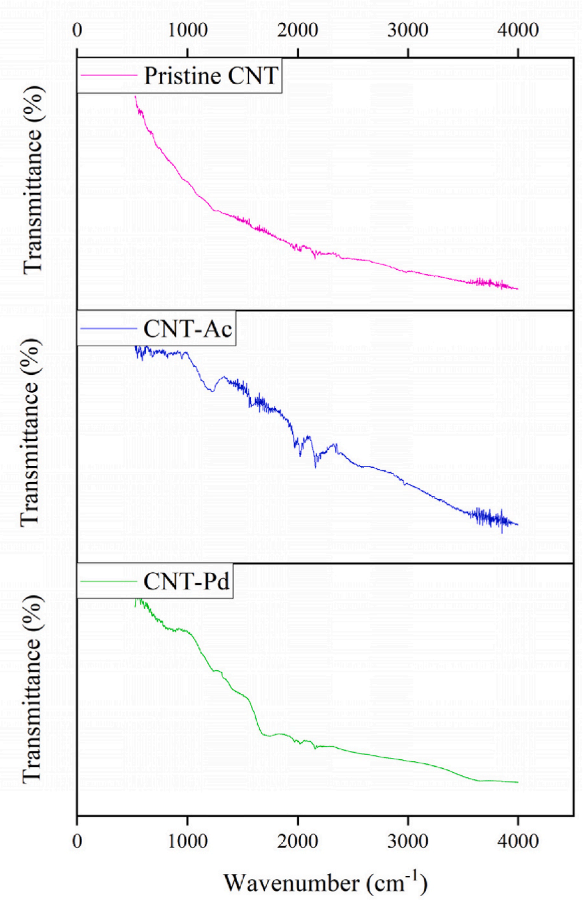
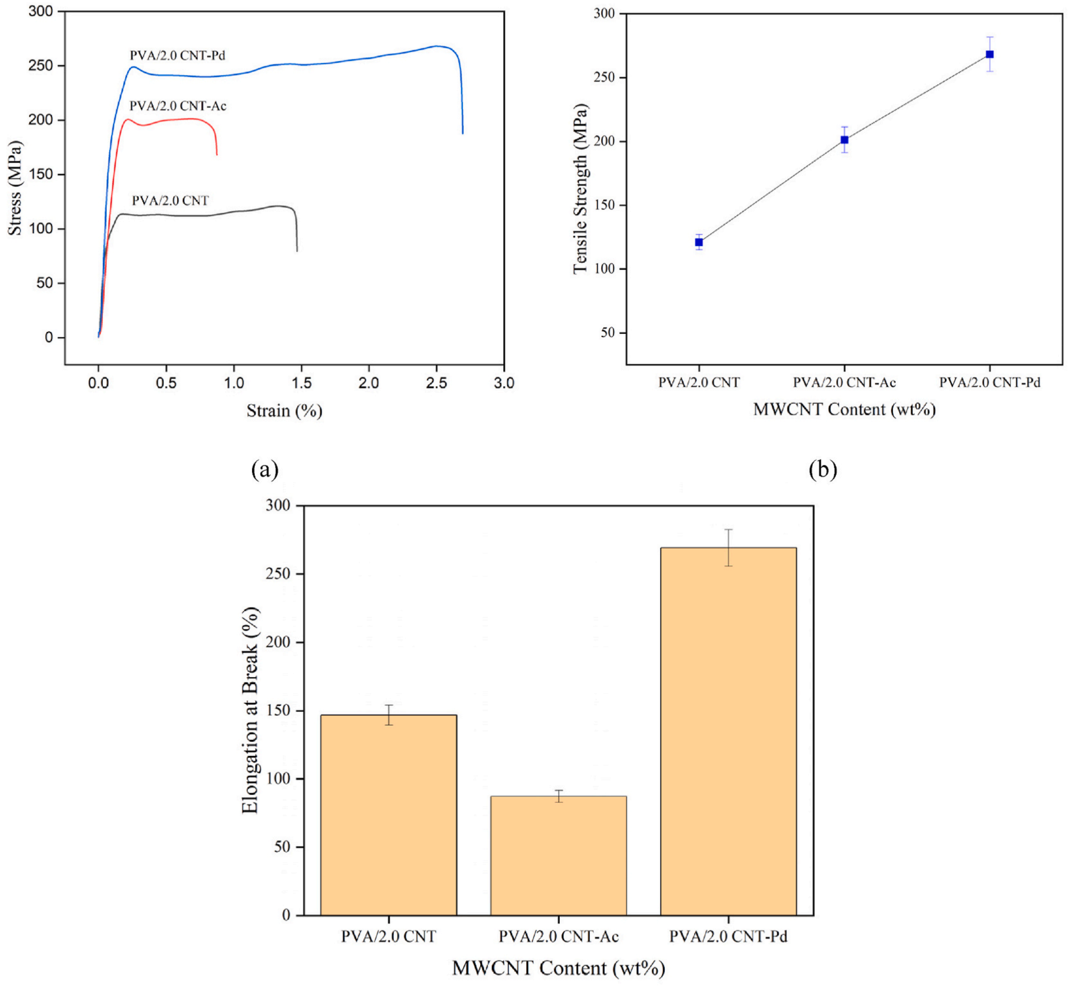


Fig. 7. FTIR spectra of pristine CNT, CNT-Ac, and CNT-Pd.

3.7. *Mechanical properties of PVA/surface modified CNT composite films*

Fig. 8(a) and (b) illustrate stress-strain curves and tensile strength of PVA/2.0 CNT, PVA/2.0 CNT-Ac, and PVA/2.0 CNT-Pd composite films. The tensile strength of 2.0 wt% CNT reinforced PVA composite increased as CNTs were acid treated and further increased on surface modification with polydopamine. This verifies a better interaction between PVA and surface modified CNTs compared to PVA and pristine CNTs. Fig. 8(c) shows the increased ductility of PVA/2.0 CNT-Pd compared to PVA/2.0 CNT though elongation was initially decreased after acid treatment due to CNTs' surface roughening and the attached functional groups. The increased elongation might be due to the enhanced interfacial interaction between the nanotubes and PVA matrix on surface modification of CNTs with polydopamine [23]. Polydopamine coating served as a strengthening agent, which created a continuous network to reduce surface damage under stress [45]. The polydopamine coating strengthens the nanotubes' structural integrity and stops them



(a) (b)

(c)

Fig. 8. (a) Stress-strain curves, (b) tensile strength, and (c) elongation at break of pure and surface modified CNT reinforced PVA films.

from slipping or pulling away from the matrix during deformation. A more uniform distribution of CNTs in the film is the result of the coating's assistance in dispersing individual nanotubes and preventing their aggregation.

The addition of functional groups to the CNT surface during polydopamine treatment encouraged physical and chemical interactions between the nanotubes and the matrix, which improved the film's mechanical properties. On the other hand, CNTs may experience surface functional group loss or structural degradation because of acid exposure. The integrity and mechanical qualities of the CNTs can be preserved, and acid-induced damage can be prevented by polydopamine treatment. Moreover, acid treatment with strong acids might oxidize the surface of CNTs as well as increase surface roughness and chemical reactivity by introducing defects to the nanotube's surface [46]. As a result, compared to untreated CNTs, the acid treated CNTs showed a lower elongation property. Again, polydopamine coating may have increased surface area, reduced surface roughness, and added new functional groups. The CNTs and PVA matrix interacted more favorably because of this treatment, enhancing load transfer and stress distribution.

Table 2
DSC data for PVA/surface modified CNT composite films.

Sample	T_g (° C)	T_m (° C)	T_c (° C)
PVA/2.0 CNT	86	225	188
PVA/2.0 CNT-Ac	71	228	184
PVA/2.0 CNT-Pd	85	226	189

3.8. Melting and crystallization behaviors of PVA/surface modified CNT composite films

The DSC result of acid and polydopamine treated CNT films are presented in Table 2 and Fig. 9 which show that acid treatment reduced both T_g and T_c. Physical and chemical cross-linking agents, moisture, salts, acids, or colloidal matters significantly influence the temperature shifting of PVA composites [47]. T_g of the film and overall structural integrity might be affected by the acid treatment. The defects or modifications introduced after acid treatment may be responsible for a greater decrease in T_g. On the other hand, when CNTs are treated with polydopamine, coating layer serves as a protective coating resulting in less decrease in T_g for PVA/2.0 CNT-Pd compared to PVA/2.0 CNT-Ac.

The value of T_m slightly increased for both PVA/2.0 CNT-Ac and PVA/2.0 CNT-Pd. CNT-Ac have functional groups, such as carboxylic acids (-COOH), added to their surface which can cause esterification due to their interaction with the hydroxyl groups (-OH) of PVA. A higher level of molecular ordering and crystallinity in the PVA matrix may come from the esterification reaction between CNT-Ac and PVA, raising the melting point of the film [48]. Polydopamine present on the surface of CNTs can interact with the CNT surface because of its aromatic and quinone-like functional groups and increase the difficulty of heat diffusion into CNTs. This can raise the melting point of the film here as well.

The surface functional groups acquired during acid treatment (carboxyl or hydroxyl groups), while meeting the PVA matrix, may disrupt the hydrogen bonding of the polymer chain and alter the crystallization process. The presence of the functional groups may have hampered the polymer chain's mobility, hence, are responsible for the decreased crystallization temperature of PVA/2.0 CNT-Ac. On the other hand, CNTs with polydopamine coatings have improved interactions with the PVA matrix, resulting in greater CNT dispersion and alignment within the polymer matrix [49]. This enhanced polymer chain mobility and crystallization behavior improved interfacial adhesion and alignment, raising the crystallization temperature of the PVA/2.0 CNT-Pd film.

3.9. Thermal stability of PVA/surface modified CNT composite films

The thermal decomposition characteristics of pure PVA and modified CNT reinforced PVA films were analyzed using TGA (Fig. 10 (a)). Compared to PVA/2.0 CNT composite film, PVA/2.0 CNT-Ac resulted in a 6° drop in the initial decomposition temperature (Fig. 10(b)). This drop can be attributed to the increased vulnerability of composites to thermal breakdown due to introduction of defects or modifications in nanotube structure by acid treatment [50]. On the other hand, the initial decomposition temperature of the PVA/2.0 CNT-Pd was increased by 16° compared to PVA/2.0 CNT. Here, polydopamine coating might act as a barrier, preventing contact between CNTs and surrounding polymer matrix as well as enhancing thermal stability of the film. A similar result was reported where the addition of polydopamine-coated CNTs in UHMWPE and Elium improved the thermal stability of the matrix [23].

3.10. UV–vis spectroscopy of PVA/surface modified CNT composite films

Fig. 11 (A) presents the difference in transmittance for PVA/2.0 CNT, PVA/2.0 CNT-Ac, and PVA/2.0 CNT-Pd films. It's interesting to note that the surface modification of CNTs improves PVA's UV-shielding capability. PVA/2.0 CNT-Ac and PVA/2.0 CNT-Pd films provide transmittances of 11 % and 9 %, respectively. Compared to pure PVA, an improvement of 86 % and 88 % has been achieved for PVA/2.0 CNT-Ac and PVA/2.0 CNT-Pd films, respectively. Similar result was reported, where optical absorbance was found to be increased with increasing GO content in the PVA matrix [51]. PVA/CNT's UV-shielding effectiveness is improved by two things: (a) by evenly dispersed CNTs, which are capable of efficiently absorbing UV light and converting their photon energy to heat; and (b) since CNTs and PVA matrix have a significant hydrogen association at the interface, which encourages the creation of a broad interface and

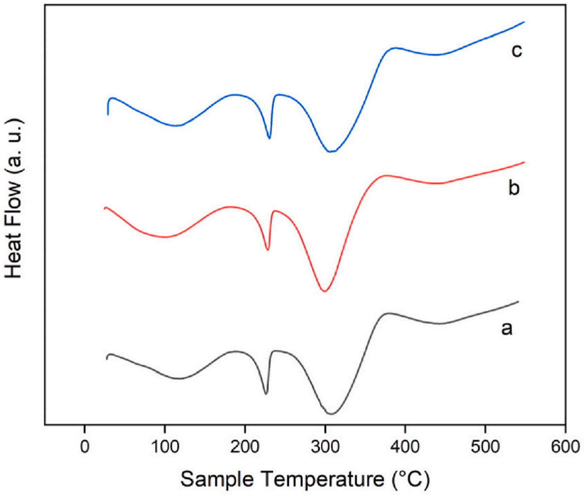
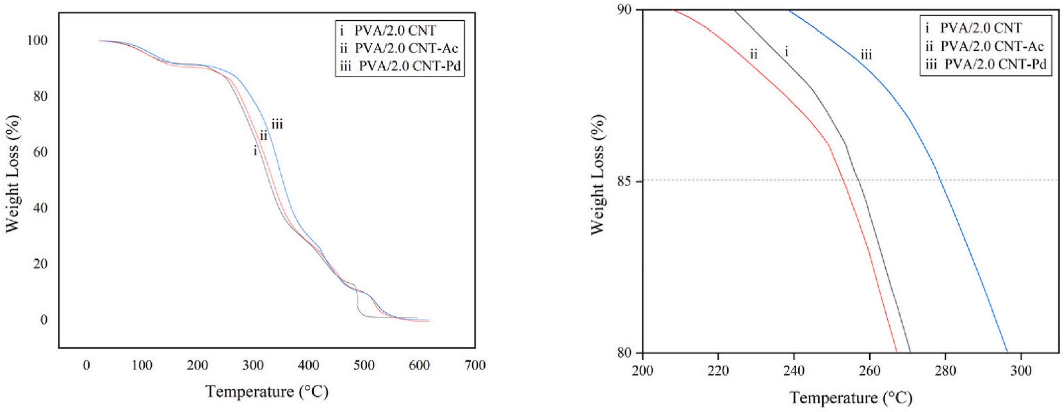


Fig. 9. DSC curves of a) PVA/2.0 CNT, b) PVA/2.0 CNT-Ac, and c) PVA/2.0 CNT-Pd composite films.



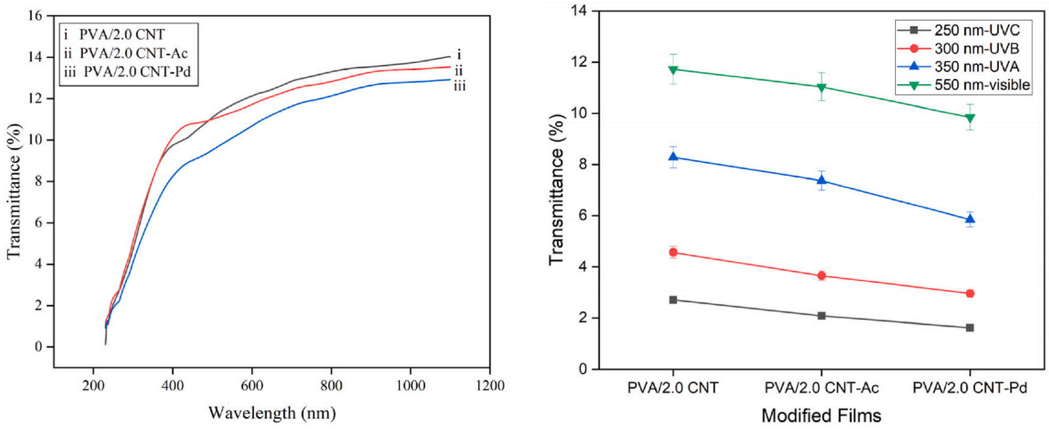
(a)   (b)

Fig. 10. (a) TGA curves and (b) initial decomposition temperature of pure and surface modified CNT reinforced PVA films.

consequently, the results scattering of UV radiation near the interface [52]. Meanwhile, distinctive porous structure and large surface area of CNTs are advantageous to the absorption and reflection of UV radiation; therefore, the incorporation of polydopamine-modified CNTs noticeably enhanced the PVA matrix's capacity to block UV rays. To assess the effectiveness of UV shielding, the transmittance of PVA/modified CNT films at different UV light wavelengths was examined. The results are given in Fig. 11 (B). Because PVA/modified CNT films display good UV light absorbance at 250 nm (UVC), 300 nm (UVB), and 350 nm (UVA), they can be perceived as UV-shielding materials. PVA/2.0 CNT film can block nearly 97.29 % UVC, 95.43 % UVB, and 91.72 % UVA, whereas PVA/2.0 CNT-Ac can block nearly 97.92 % UVC, 96.34 % UVB, and 92.63 % UVA, and PVA/2.0 CNT-Pd can block almost 98.37 % UVC, 97.04 % UVB, and 94.15 % UVA. It is clearly visible that polydopamine-modified CNT addition to PVA can significantly improve the absorbance of UV rays and form unique materials with extraordinary UV-shielding properties.

3.11. Antibacterial property of pure PVA and PVA/2.0 CNT-Pd composite films

By using the colony counting method, an antibacterial test was conducted against gram-positive *S. aureus* and gram-negative *E. coli* to evaluate the antibacterial activity of PVA and PVA/2.0 CNT-Pd. Table 3 shows the number of colonies killed by pure PVA and PVA/2.0 CNT-Pd films. It is evident that bacterial populations got smaller over time for both samples. It is seen that after 2 h, 6 h, and 24 h, pure PVA killed 12.4 %, 33.1 %, and 68.6 % of *S. aureus*, respectively. On the other hand, PVA/2.0 CNT-Pd killed 10.7 %, 37.2 %, and 74.4 % of *S. aureus* after 2 h, 6 h, and 24 h, respectively. Fig. 12(a) shows a comparison of these two samples. It is observed that just after the addition of polydopamine-modified CNT, initially the films' ability to kill gram-positive *S. aureus* was very close to that of pure PVA films, and with time, it surpassed the number of *S. aureus* killed by pure PVA. Similar performance was observed for *E. coli*. It is seen that after 2 h, 6 h, and 24 h, pure PVA killed 39.9 %, 69.6 %, and 76.3 % of *E. coli*, respectively. On the other hand, PVA/2.0 CNT-Pd killed 63.2 %, 75.9 %, and 87.4 % of *E. coli* after 2 h, 6 h, and 24 h, respectively. Fig. 12(b) shows a comparison of these two samples. It is observed that after the addition of polydopamine-modified CNTs, the films' ability to kill gram-negative *E. coli* was increased by 14.55 % at 24 h in comparison to that of pure PVA film. Antibacterial test results verify that PVA/2.0 CNT-Pd has good antibacterial activity against gram-positive *S. aureus* and gram-negative *E. coli*. It is because CNTs could reach the nuclei of the bacteria, mixing with DNA, and forming ROS (oxygen-containing reactive species), which ultimately caused cell death [47]. Antibacterial characteristics are inherent properties of polydopamine and broad-spectrum antimicrobial action of polydopamine has reportedly been observed against a variety of pathogens, including gram-positive and gram-negative bacteria [53,54]. In comparison to pure PVA, PVA/2.0 CNT-Pd film has stronger antibacterial action since it contains polydopamine. The presence of polydopamine, CNTs, and PVA may have a synergistic effect on the antibacterial activity. The antibacterial effects of polydopamine were enhanced by the antimicrobial features of CNTs, such as their capacity to damage bacterial cell membranes. Polydopamine coating of CNTs also improved their dispersion inside PVA matrix, increasing their contact with bacteria and boosting their antibacterial activity. The film's surface charge and interactions with bacteria changed by adding polydopamine and CNTs [55]. Bacteria often have a negatively charged outer membrane, whereas polydopamine and CNTs frequently have a positively charged surface. In comparison to pure PVA, the electrostatic attraction between surface of the PVA/2.0 CNT-Pd film and bacteria may have promoted improved adherence and antibacterial action. When CNTs and polydopamine came into contact, the bacterial cell membrane went through structural modifications. By piercing the lipid bilayer and damaging the membrane, polydopamine disrupted bacterial membranes. CNTs might have physically pierced bacterial membrane due to their nanoscale dimensions and sharp edges, which caused cell lysis and death. The enhanced antibacterial activity of the composite film is a result of these combined actions. Hussain et al. were also able to significantly reduce the number of familiar bacterial species such as *S. bacter*, *E. coli*, and *K. pneumonia* by functionalizing CNTs with piperazine and dopamine [53]. Layer-by-layer construction of the CNTs coated by polydopamine and polyethyleneimine also resulted in a strong thin film that displayed outstanding resistance to *E. coli* [54]. Nanocomposite films made of polydopamine-modified CNT reinforced poly

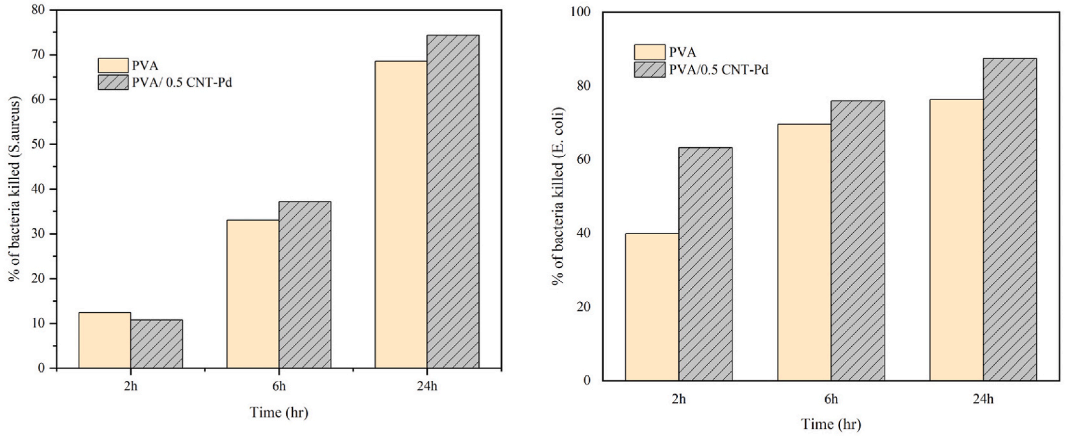


(a) (b)

Fig. 11. (a) UV–vis spectra, and (b) change in transmittance at particular UV radiation wavelengths (UVA, UVB, and UVC) of pure and surface modified CNT reinforced PVA films.

Table 3
Antibacterial test results with bacterial colonies killed.

Sample	Number of bacterial colonies in a specific time (*S. aureus*)				Number of bacterial colonies in a specific time (*E. coli*)			
	0 h.	2 h.	6 h.	24 h.	0 h.	2 h.	6 h.	24 h.
PVA	121	106	81	38	253	152	77	60
PVA/2.0 CNT-Pd	121	108	76	31	253	93	61	32
Control	121	124	150	169	253	518	615	1019



(a) (b)

Fig. 12. Antibacterial test results with bacterial colonies killed (a) *S. aureus*, and (b) *E. coli.*

(lactic acid) designed for food packaging demonstrated stronger antibacterial and antifungal activity than pure PLA [56].

4. Conclusion

This study successfully boosted the mechanical, thermal, optical, and antibacterial properties of PVA nanocomposite films through the use of polydopamine-coated CNTs, in comparison with both pristine and acid-treated CNT/PVA films. At first, pristine MWCNT was introduced to PVA matrix to evaluate its impact on the mechanical, thermal, and optical properties of the resulting nanocomposite films. After initial characterization, using optimal CNT content of 2.0 wt%, pristine CNT was treated with a mixture of H_2SO_4 and HNO_3 and later coated with a biopolymer, polydopamine. Two differently treated CNTs of 2.0 wt% were added to the PVA matrix to form PVA/modified CNT nanocomposite films and were subjected to mechanical, thermal, and optical characterization. PVA/2.0 CNT-Pd films have shown a 22.41 % increase in tensile strength compared to the PVA/2.0 CNT-Ac films. Enhanced strain property of PVA/2.0 CNT-Pd films proved better interaction between PVA and CNT-Pd than that between PVA and CNT-Ac. Compared to pure PVA, improved thermal stability resulted from CNT-Pd addition, as an increase of 12 °C in temperature was recorded. The transmittance of PVA/2.0 CNT-Ac, and PVA/2.0 CNT-Pd films is reduced by 84 % and 86 %, respectively, compared to pure PVA, indicating improved dispersion as the CNT nanoparticles' distinctive porous structure and large surface area are advantageous to the absorption and reflection of UV radiation. The polydopamine-modified CNTs can be added to PVA to improve the absorbance of UV rays and create a unique material with exceptional UV-shielding properties, as PVA/2.0 CNT-Pd films can block almost 98.37 %, 97.04 %, and 94.15 % of UVC, UVB, and UVA, respectively. PVA/2.0 CNT-Pd killed 10.7 %, 37.2 %, and 74.4 % of *S. aureus* after 2 h 6 hrs., and 24 h, respectively. It also killed 63.2 %, 75.9 %, and 87.4 % of *E. coli* after 2 h, 6 h, and 24 h, respectively. PVA/polydopamine-modified CNT films' ability to kill gram-negative *E. coli* was increased by 14.55 % at 24 h compared to pure PVA. Therefore, PVA/2.0 CNT-Pd can be a suitable candidate in food packaging.

CRediT authorship contribution statement

Mahjabin Moon: Writing – original draft, Methodology, Investigation, Formal analysis. **Samiya Rahman Mim:** Writing – review & editing. **Md. Muktadir Billah:** Writing – review & editing, Supervision, Resources, Conceptualization. **A.K.M. Masud:** Writing – review & editing, Supervision, Conceptualization.

Data availabilty statement

No data was applied for the study described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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