Interfacial and mechanical performance of chemically modified high content MWCNT/PEEK thermoplastic composites

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Abstract

It is difficult to increase the content of carbon nanotubes in carbon nanotubes/polyether ether ketone (CNTs/PEEK) thermoplastic composites prepared by doping carbon nanotubes into highly viscous PEEK resin using conventional methods. In this paper, a multi-walled carbon nanotubes/PEEK (MWCNT/PEEK) thermoplastic composite film with high MWCNTs content is prepared by vacuum suction filtered and hot-pressing methods. The microstructure and interfacial bonding performance of chemically modified and unmodified composites in the form of films are analyzed by molecular dynamics simulation and experiment. The results show that MWCNT can significantly improve the crystallinity of PEEK resin. Compared with the MWCNT/PEEK composites without chemical modification, the MWCNT-COOH/PEEK-OH composite film has a denser structure, and the tensile strength and elastic modulus are increased by 94.5% and 15%, respectively. The MWCNT-COOH/PEEK-OH composite films are expected to be used for interlaminar mechanical performance enhancement of CF/PEEK high-performance thermoplastic composites, which are widely used in aerospace.

1 Introduction

The forming of CF/PEEK thermoplastic composites by automated fiber placement (AFP) in-situ consolidation method has a great attraction for aerospace [1–4]. However, due to the short time of heating and pressurizing the CF/PEEK prepreg during the rapid laying of AFP, the PEEK resin with a high melting point and high viscosity cannot fully flow and diffuse in a short time, causing a thin layer of the resin-rich region between the plies of the formed CF/PEEK laminate [5, 6]. There is no carbon fiber reinforcement in the resin-rich region, and only the resin matrix plays the role of bonding and transferring load, resulting in poor interlaminar mechanical performance [7]. Zhang et al. [8] and Sun et al. [9] found that the mechanical performance can be enhanced in situ using CNTs reinforced materials. However, if CNTs are doped directly into PEEK resin, agglomeration tends to occur resulting in a non-uniform distribution of CNTs, which is attributed to the strong van der Waals forces and electrostatic forces between them [10, 11]. In addition, both CNTs and PEEK resin have a chemically inert surface. If they are simply doped together, there is a problem of poor interfacial bonding performance [12, 13]. Therefore, it is necessary to develop a CNTs/PEEK composite material to solve the above problems.

Regarding the interfacial bonding performance between CNTs and resin matrix, chemical modification can be used to make CNTs and PEEK surface modified with oxygen-containing functional groups, which can generate polar bonds between them to enhance the interfacial bonding performance [14, 15]. Zhu et al. [16] amidated PEEK and acylated CNTs to improve their bonding performance. Lv et al. [17] modified -COOH and -OH functional groups on CNTs and PEEK resin, respectively. The esterification reaction occurred between the functional groups to improve the interfacial bonding performance. As for the non-uniform distribution of CNTs in PEEK resin due to agglomeration, buckypaper (BP) are the macroscopic two-dimensional material made up of CNTs, which can effectively solve the problem [18]. The CNTs in BP are uniformly distributed and independent in any direction, generating continuous stress transfer carriers [19, 20]. The preparation methods for BP have vacuum suction filtration (VSF) and chemical vapor
deposition (CVD). The BP made by the CVD method is dense and has a small internal pore size, which means it is unsuitable for reinforcing polymer composites [21, 22]. The VSF method can prepare BP with a large pore size and loose structure. Meanwhile, this method is easy to control the thickness of the film and can prepare the film with mixed composition, so the VSF method still attracts wide attention [23, 24]. The methods to combine BP with polymers to form composites are hot pressing [25], infiltration [26], and soaking [27]. Since PEEK resin has a high melting point and high viscosity and is chemically inert (only dissolves in strongly acid solution), it is impossible to prepare polymer composites by infiltration and soaking methods. Therefore, the surface chemically modified CNTs and PEEK powder are mixed homogeneously and prepared into composite films by VSF and hot-pressing methods, which can solve the problem of fully infiltrating the highly viscous PEEK resin into the interior of the BP. Moreover, the chemically modified CNTs and PEEK can generate polar bonds to improve the interfacial bonding performance. Particularly, CNTs/PEEK composite films used as interlaminar reinforcements for CF/PEEK laminates do not suffer from resin-to-reinforcement compatibility problems. However, the PEEK resin content in CNTs/PEEK composite films should be as minimal as possible in order not to introduce additional resin content in the interlaminar. A small amount of PEEK resin in the CNTs/PEEK composite films only plays the role of adhesion between CF/PEEK plies. The formation of CNTs/PEEK composite films with high CNTs content using a buckypaper preparation method has not been reported in the literatures.

In this paper, a method for the preparation of chemically modified and unmodified MWCNT/PEEK composite films with high MWCNT content is proposed. The micromorphology, composition, interfacial and mechanical performance of the MWCNT/PEEK composite films is analyzed based on molecular dynamics and experimental methods.

2 Molecular Dynamics Simulations

2.1 Molecular modeling

The microscopic interface model of MWCNT and PEEK are developed using Materials Studio software. Figure 1 (a) shows the MWCNT and PEEK microscopic interface model without chemical modification, which is abbreviated as MWCNT/PEEK. The MWCNT is selected as (6,6) armchair type with 36.89 Å length and 3.347 Å wall spacing. The PEEK long-chain molecular model is chosen to be 10 degrees of polymerization, after which it is geometrically optimized in 20,000 steps under the COMPASS force field and Smart algorithm to obtain the optimal conformation of the PEEK long-chain molecule [17]. Then MWCNT/PEEK amorphous structures with dimensions of 50 × 50 × 50 Å and a density of 1.3 g/cm³ are built using the Construction and Packing methods in the Amorphous Cell module [28], in which 29 long chains of PEEK are filled. Figure 1 (b) shows the chemically modified MWCNT/PEEK microscopic interface model. the MWCNT surface is modified with carboxylation (-COOH), and 14 carboxyl groups are randomly added to its molecular model surface. The PEEK surface is modified with hydroxylation (-OH), replacing the ketone group (C = O) with a hydroxyl group at six random positions in the long chain of
PEEK. The number of modified groups depends on the degree of functionalization provided by the manufacturer. The microscopic interface model of chemically modified MWCNT-COOH and PEEK-OH is developed in the same way as the unmodified one and is abbreviated as MWCNT-COOH/PEEK-OH. The molecular kinetic equilibrium is required to make the established microscopic interface model with minimum energy and stable structure. (Detailed kinetic equilibrium steps are provided in the supporting materials.)

2.2 Interface microstructure

In molecular dynamics models, the stacking state of PEEK molecular chains around MWCNT determines its microscopic interfacial structure. The radial distribution function (RDF), relative concentration (RC), mean square displacement (MSD), and free volume fraction (FFV) can be used in molecular dynamics to characterize the stacking state of PEEK around MWCNT [29–31]. (Detailed descriptions of RDF, RC, and MSD are provided in the supporting materials.)

Figure 2 (a) is the RDF curves for the MWCNT/PEEK and MWCNT-COOH/PEEK-OH models, depicting the average number of PEEK and PEEK-OH molecules appearing around MWCNT and MWCNT-COOH, respectively. In the range of 0.9–1.2 Å, only the MWCNT-COOH/PEEK-OH model shows a peak indicating a closer distribution of PEEK-OH with MWCNT-COOH. In the range of 1.3–1.6 Å and 2.3–2.6 Å, the peaks appear in the both MWCNT/PEEK and MWCNT-COOH/PEEK-OH models. However, the peak intensity of MWCNT-COOH/PEEK-OH is higher than that of the MWCNT/PEEK model, indicating that there is more PEEK-OH around MWCNT-COOH and the PEEK-OH is more tightly packed around MWCNT-COOH.

Figure 2 (b1) and (b2) are the RC curves for the distribution of PEEK and PEEK-OH around MWCNT and MWCNT-COOH, respectively. In MWCNT/PEEK model, the MWCNT is located at the center with a diameter of about 15 Å and a model edge length of 50 Å. Therefore, the middle region (17.5 ~ 32.5 Å) is the MWCNT, the region where the PEEK tends to grow outward on both sides is defined as the interface region between the MWCNT and PEEK, and the outermost region is pure PEEK. Each region of the MWCNT-COOH/PEEK-OH model is divided in the same way as MWCNT/PEEK model. The relative concentrations of the PEEK and PEEK-OH distributions are calculated along the two orientations of the models X and Y, respectively. It can be found that the relative concentration of MWCNT-COOH/PEEK-OH is higher than that of the MWCNT/PEEK model in the interface region, indicating a stronger mutual attraction between PEEK-OH and MWCNT-COOH.

Figure 2 (c1) and (c2) are the MSD and diffusion coefficient of PEEK and PEEK-OH molecular. Figure 2 (c1) shows that the PEEK-OH has a lower mobility than PEEK. In the sharply rising section of the MSD curve (0 ~ 1 ps), the slopes of the MWCNT/PEEK and MWCNT-COOH/PEEK-OH models at this stage are obtained by linear fitting as 0.53 and 0.44, with determination coefficients of 0.97 and 0.94, respectively. The diffusion coefficients of 0.088 and 0.073 for PEEK and PEEK-OH are calculated from Eqs. 3 in the supplemental material, indicating that PEEK-OH has lower diffusivity than PEEK because PEEK-OH stacks more tightly around MWCNT-COOH and the interactions are stronger, limiting the diffusion of PEEK-OH molecular.
The FFV is the ratio of the volume of voids between molecular chain segments to the total volume in the model. Usually, the smaller the FFV, the stronger the interactions between molecules and the denser the stacking between molecular [32]. The FFV of the MWCNT/PEEK and MWCNT-COOH/PEEK-OH models are obtained by molecular dynamics calculations as 12.3% and 11.7%, respectively, as shown in Fig. 2 (d). Compared to the MWCNT/PEEK model, the FFV of MWCNT-COOH/PEEK-OH is smaller, indicating a denser stacking between MWCNT-COOH and PEEK-OH. It is also demonstrated that the interaction force between MWCNT-COOH and PEEK-OH limits the diffusivity of the PEEK-OH molecular, which is tightly packed around MWCNT-COOH, making the model denser overall.

### 2.3 Interface bonding performance

The interfacial bonding performance between molecules can be characterized by interfacial adsorption energy and cohesion energy density in molecular dynamics simulations [17, 33]. In the MWCNT/PEEK model, the interfacial adsorption energy is the interaction energy between MWCNT and PEEK. The interfacial adsorption energy \( E_{\text{interaction}} \) is calculated as follows [28]:

\[
E_{\text{interaction}} = E_{\text{total}} - (E_{\text{mwcnt}} + E_{\text{peek}})
\]

where \( E_{\text{total}} \) is the total potential energy of the model, \( E_{\text{mwcnt}} \) is the potential energy of the MWCNT, and \( E_{\text{peek}} \) is the potential energy of the PEEK resin.

Figure 3 is the interfacial adsorption energy results for the MWCNT/PEEK and MWCNT-COOH/PEEK-OH models. The interfacial adsorption energies of the MWCNT/PEEK and MWCNT-COOH/PEEK-OH models are \(-1135.3\) Kcal/mol and \(-4555.9\) Kcal/mol, respectively, where the negative values of the results indicate the existence of attractive interaction forces between MWCNT and PEEK. The more negative the value of the interaction energy (the larger the absolute value), the stronger the interfacial interaction, indicating better bonding performance. Due to the more negative interaction energy of the MWCNT-COOH/PEEK-OH model, MWCNT-COOH/PEEK-OH has better interfacial bonding performance than that of the MWCNT/PEEK model, which is attributed to the chemically modified MWCNT-COOH and PEEK-OH molecules add more oxygen-containing polar functional groups. MWCNT-COOH/PEEK-OH model not only has \( \pi-\pi \) conjugation effect but also increases the hydrogen bonding interactions between molecules, making their bonding performance stronger. The effect of hydrogen bonding can also be seen from the non-bonding energy in Fig. S1, which is more negative for the MWCNT-COOH/PEEK-OH model compared to the MWCNT/PEEK model.

The cohesion energy between molecules \( E_{\text{coh}} \) is the average energy required to separate all molecules to an infinite distance, while the cohesion energy density is the cohesion energy between molecules per unit mol. Therefore, the cohesion energy density can characterize the interaction forces between molecules. A higher cohesion energy density indicates a stronger bonding force between molecules. The cohesion energy density is calculated as follows [32]:

\[
E_{\text{coh}} = E_{\text{inter}} = E_{\text{total}} - E_{\text{intra}}
\]
where $E_{\text{inter}}$ is the intermolecular energy, $E_{\text{intra}}$ is the intramolecular energy, and $c$ is the molarity. The cohesion energy densities of the MWCNT/PEEK and MWCNT-COOH/PEEK-OH models are 485.6 J/cm$^3$ and 510.5 J/cm$^3$, respectively, calculated by molecular dynamics, indicating stronger molecular interactions between MWCNT-COOH and PEEK-OH after chemical modification.

3 Experiments

3.1 Materials and Methods

The MWCNT and MWCNT-COOH powders with diameters of 10–30 nm, lengths of 10–30 µm, and specific surface areas of 150–200 m$^2$/g are purchased from Jiacai Technology Co., Ltd (in Chinese). The PEEK and PEEK-OH powders in the size range of 800 ~ 1200 are supplied by Qiang Shong Plasticizing Raw Materials Co., Ltd (in Chinese). Triton (X-100) is a surfactant for ultrasonic dispersion of MWCNT and PEEK powders, purchased from Sinopharm Chemical Reagent Co., Ltd (in Chinese). The organic microporous membrane of hydrophilic polytetrafluoroethylene (PTFE) with an average pore size of 0.45 µm is used for the filtration membrane, which is supplied by Haining Delv New Material Technology Co., Ltd (in Chinese).

Figure 4 shows a schematic diagram of the preparation process of MWCNT/PEEK composite films. The chemically modified MWCNT-COOH/PEEK-OH composite films are prepared in the same way. The homogeneous mixed solution of MWCNT and PEEK powders is made by mechanical stirring and ultrasonic dispersion. The dispersions solution is vacuum suction filtered (VSF) and vacuum dried to obtain hybrid films preform of MWCNT and PEEK. Then, the final MWCNT/PEEK composite film is made by the hot press technique. The thickness and carbon nanotube content of both MWCNT/PEEK and MWCNT-COOH/PEEK-OH composite films are 0.1 ~ 0.13 mm and 50 wt. %. (The detailed preparation steps are provided by the supporting materials.)

3.2 Performance characterization methods

The micromorphology of the samples is observed by scanning electron microscopy (SEM) with a HELIOS NanoLab 600i from FEI, USA. Since PEEK resin is non-conductive, the samples need to be treated with gold spray for 5 min before SEM observation. The composition of the samples is analyzed by a Nicolet is50 Fourier infrared spectrometer (FTIR) and an ESCALAB 250Xi X-ray photoelectron spectrometer (XPS) from ThermoFisher, U.S.A. The FTIR range is 500–4000 cm$^{-1}$; the XPS uses an Al Kα target radiation source with a test voltage of 15 kV, a power of 150 W, an energy level of 20.0 eV, and a step of 0.05 eV. In addition, the content of the sample components is measured by an EDS spectrometer from OXFORD (UK). The pore size of the samples is tested by N$_2$ adsorption experiments, which are measured at 77 K on a Quantachrome QuadraSorb Station 3 instrument. The distribution range of pore size can be obtained from the adsorption branch of the N$_2$ adsorption isotherm by Barret-Joyner-Halenda (BJH) method [34]. The crystallinity of the samples is conducted by X-ray diffraction (XRD, Bruker, Germany)
and differential scanning calorimeter (DSC, NETZSCH, USA). The Cu Kα radiation is selected for XRD experiments. The tube voltage and current were 40 kV and 150 mA, respectively. The scanning speed and range were 8°/min and 5°~60°, respectively. The tensile test of the samples is carried out using an Instron 3343 tensile apparatus with a load cell of 20 N, at a constant loading speed of 0.5 mm/min. The dimensions of the tensile test specimen of the composite film are 30×10 mm.

3.3 Microstructure and compositions

Figure 5 (a) and (b) show the micromorphology of MWCNT and MWCNT-COOH powders. They both appear as agglomerated blocks because the powders are directly adhered to the conductive tape for SEM observation without dispersion, while carbon nanotubes are highly prone to agglomeration under the action of van der Waals forces and electrostatic forces. However, the agglomeration of MWCNT-COOH is more serious than that of MWCNT powder, because the presence of carboxyl functional groups on the surface of MWCNT-COOH by chemical modification, and the formation of hydrogen bonds between functional groups makes the intermolecular force stronger, resulting in more serious agglomeration. Figure 5 (c) and (d) show the micromorphology of PEEK and PEEK-OH powders. They both appear as irregular particles and the particle size is mainly distributed in the range of 10–20 μm. The average oxygen element content of MWCNT, MWCNT-COOH, PEEK, and PEEK-OH powders is 20.9%, 25.2%, 19.5%, and 20.8%, respectively. The oxygen element content of MWCNT-COOH and PEEK-OH powders is higher than that of MWCNT and PEEK powders, which is attributed to the chemical modification that increases the oxygen-containing functional groups, making the oxygen element content increase.

Figure 6 is the micromorphology of the prefabricated films. It can be seen from the surface micromorphology that PEEK and PEEK-OH powders are dispersed on the surface of the prefabricated films, respectively. Meanwhile, MWCNT and MWCHT-COOH are adsorbed on the resin particles. As a result, the macroscopic morphology of the surface of the prefabricated films in Fig. 6 (a) and (b) show a light white layer of resin powder. The presence of PEEK and PEEK-OH powders can also be seen in the cross-sectional micromorphology, indicating that the composite film preparation method proposed in this paper can make carbon nanotubes and PEEK powders form a uniformly mixed structure with each other and solve the problem that the conventional method cannot make the highly viscous PEEK resin infiltrate into the interior of BP.

Figure 7 is the micromorphology of the final composite film obtained from the prefabricated film after the hot press process. It can be seen from the surface micromorphology that the PEEK and PEEK-OH powders have fully melted and cover the surface of the composite film. Meanwhile, the macroscopic morphology of the composite film shows the glossy surface of PEEK resin, which indicates that the resin powder is sufficiently melted during the hot press process. However, there are some minor potholes defects in the surface micromorphology, which are probably attributed to the failure of the molten highly viscous PEEK resin to fill the air locations that cannot be expelled in the closed mold during the hot press process. In contrast to the loose structure in the cross-sectional morphology of the prefabricated films in Fig. 6 (c) and (d), a dense composite film is formed after the hot press process, as shown in Fig. 7 (c) and (d). Meanwhile, the melted PEEK resin adhered to the carbon nanotubes can be seen in the high
magnification of the cross-sectional morphology. Since the section morphology observation samples are prepared by scissor cutting method, it caused the fracture inside the MWCNT/PEEK composite film (Fig. 7 (c)), because the unmodified MWCNT and PEEK powder surfaces are inert and the bonding performance between them is poor to resist the shear force during the cutting process. However, the same preparation method of MWCNT-COOH/PEEK-OH composite films does not produce severe fractures due to the presence of hydrogen bonds formed between the polar oxygen-containing functional groups, and possibly even a small amount of ester bonds making the bond between MWCNT-COOH and PEEK-OH tighter and can resist shear forces without damage. The comparison of cross-sectional micromorphology shows that MWCNT-COOH/PEEK-OH is denser than MWCNT/PEEK composite films.

Figure 8 is the N$_2$ adsorption isotherm. MWCNT/PEEK and MWCNT-COOH/PEEK-OH have the same type IV adsorption curve and the H3 hysteresis ring, which are commonly found in aggregates with lamellar structures, indicating irregular mesopores or macropores in the pore structure. The average pore sizes of MWCNT/PEEK and MWCNT-COOH/PEEK-OH composite films are calculated by the BJH method to be 24.5 nm and 20.3 nm, respectively. Meanwhile, the pore size distribution of MWCNT-COOH/PEEK-OH composite films is smaller mainly below 50 nm, while the maximum pore size of MWCNT/PEEK composite films can reach about 80 nm. As a result, the MWCNT-COOH/PEEK-OH composite film has a denser structure.

To verify whether the MWCNT and PEEK powders are chemically modified with -COOH and -OH functional groups, chemical composition analysis is performed using XPS and FTIR methods. Figure 9 (a) and (b) show the XPS diffraction curves of MWCNT and MWCNT-COOH powders. Four diffraction peaks appear in the C1 spectra of MWCNT-COOH powder at 284.8, 286.0, 287.8, and 288.5 eV binding energy positions corresponding to C-C, C-O, C = O, and O-C = O chemical bonds, respectively [35, 36]. The O-C = O corresponds to the -COOH functional group, while no diffraction peaks of the O-C = O appear in the MWCNT powder. The appearance of C-O and C = O in MWCNT powder is mainly because MWCNT is easily contaminated by oxidation in the air [37]. The content of different chemical bonds can be obtained by calculating the percentage of each frontal area. The content of C = O and O-C = O of MWCNT-COOH powder is 8.49% and 3.07%, respectively, which is larger than that of MWCNT powder. Meanwhile, the ratios of oxygen to carbon element content of MWCNT and MWCNT-COOH powders are calculated in the full spectrum as 0.05 and 0.09, respectively. Because of the presence of a carbon-oxygen double bond in -COOH, the carbon-oxygen double bond content and the oxygen-carbon ratio of MWCNT-COOH powder are higher than those of MWCNT powder. Figure 9 (c) shows the FTIR diffraction curves. The FTIR diffraction curves of MWCNT and MWCNT-COOH powders are the same because of the black color of carbon nanotubes, which has a strong absorption of infrared light. However, local amplification in the wavenumber ranges from 1000 to 2000 cm$^{-1}$ can find small peaks at 1753 and 1120 cm$^{-1}$ positions of MWCNT-COOH powder, corresponding to stretching vibrations of C = O and O-C = O chemical bonds, respectively [38, 39], where the carbon-oxygen double bond corresponds to the -COOH functional group. Furthermore, the EDS analysis in Fig. 2 also indicates that the MWCNT-COOH powder has a higher oxygen
content, which is attributed to the increased oxygen content by the -COOH functional group. Therefore, the above analysis indicates that MWCNT-COOH powder is modified with the -COOH functional group.

Figure 10 is the XPS and FTIR diffraction curves of PEEK and PEEK-OH powders. Figure 10 (a) and (b) show the presence of C-C, C-O, and C = O in the C1 spectra. The calculated C-O and C = O contents show that the C = O content of PEEK-OH powder is 3.46% lower than that of PEEK powder which is 5.08%. The C-O content of PEEK-OH powder is 25.23% higher than that of PEEK powder which is 22.61%. Because the hydroxylation modification requires the carbon-oxygen double bond of the carbonyl group in PEEK to be opened to form a carbon-oxygen single bond, the C-O content of PEEK-OH powder is higher than that of PEEK, while the C = O content is lower than that of PEEK. In addition, the oxygen-to-carbon ratio of 0.19 for PEEK-OH powder is like that of 0.17 for PEEK, which is consistent with the EDS results in Fig. 2, indicating that hydroxylation does not have a significant effect on the oxygen content of PEEK. The O1 spectra show an O-H peak at 532.2 eV for the PEEK-OH powder [40] and the C = O content of the PEEK-OH powder is less than that of PEEK (as shown in Fig. 10 (c) and (d)). Meanwhile, the FTIR curve in Fig. 10 (e) shows that PEEK-OH powder shows a peak at 3430 cm$^{-1}$ compared to PEEK, which corresponds to the stretching vibration of the -OH functional group [41]. Therefore, the above analysis suggests that the PEEK-OH powder is modified with -OH functional groups.

Figure 11 shows the XPS and FTIR diffraction curves of MWCNT/PEEK and MWCNT-COOH/PEEK-OH composite films. The C1 spectra show an additional O-C = O peak for MWCNT-COOH/PEEK-OH than for MWCNT/PEEK composite films. In the FTIR diffraction curves, the MWCNT-COOH/PEEK-OH composite films show small O-C = O peaks at positions 1012 and 1100 cm$^{-1}$. The O-C = O corresponds mainly to the -COOH functional group, but since the -COOH and -OH functional groups may produce a little ester bond, which also corresponds to the O-C = O peak. Furthermore, the O1 spectra of MWCNT-COOH/PEEK-OH composite films show no O-H peaks compared to PEEK-OH powder, but instead O-C = O peaks at the 534.5 eV position, which may be attributed to the occurrence of esterification reactions causing the breakdown of O-H chemical bonds. Meanwhile, Diez-Pascual et al [42] found that the O-C = O at the 534.5 eV position contains ester bonds formed by esterification reactions. Therefore, a small amount of ester bonds may have been generated in MWCNT-COOH/PEEK-OH composite films.

### 3.4 Crystallinity and mechanical performance

For PEEK thermoplastic composites with semi-crystallinity, the crystallinity influences the mechanical performance of the components. Since the charge densities of crystalline and uncrystallized regions within the substance are different, the XRD test can obtain diffraction peaks corresponding to crystalline and amorphous regions. An intensity factor is used to correct the integrated intensity of the different diffraction peaks. Then, the integrated intensity of the crystalline diffraction peaks is ratioed to the total integrated intensity of all diffraction peaks to obtain the relative crystallinity of the substance. Figure 12 is the XRD diffraction peaks of MWCNT powder, PEEK powder, MWCNT/PEEK, and MWCNT-COOH/PEEK-OH composite films. The PEEK powders show four crystalline diffraction peaks at positions 18.8°, 20.7°, 22.9°, and 28.9° corresponding to (110), (111), (200), and (211) crystalline planes [43, 44]. MWCNT
powders show (002) crystalline diffraction peaks at the 25.1° position [45]. MWCNT/PEEK and MWCNT-COOH/PEEK-OH composite films show crystalline diffraction peaks containing PEEK and MWCNT powders, respectively. According to the XRD splitting results (as shown in Fig. 12 (b-d)), the integrated intensities of different crystalline diffraction peaks can be obtained, and the relative crystallinity can be calculated by intensity factor correction according to the following equation $X_c$ [46],

$$X_c = \frac{I_{110} + 1.35I_{111} + 1.80I_{200} + 4.10I_{211}}{I_{110} + 1.35I_{111} + 1.80I_{200} + 4.10I_{211} + 0.91I_{\alpha}} \times 100\%$$

where $I_{hkl}$ is the integrated intensity of the crystalline diffraction peak and $I_{\alpha}$ is the integrated intensity of the amorphous diffraction peak. The relative crystallinity of the PEEK powder, MWCNT/PEEK, and MWCNT-COOH/PEEK-OH composite films are 27.98%, 45.56%, and 45.18%, respectively.

When nanoparticles are doped inside the polymer, two main factors simultaneously affect the crystallization process. One is that the nanoparticles restrict the movement and alignment of the polymer chain segments making the crystallinity less. The second is that the nanoparticles themselves become nucleation sites for crystallization within the polymer, accelerating the deposition of polymer chain segments for crystallization. These two processes occur simultaneously and the crystallization of the polymer depends on which process is dominant. The significantly higher crystallinity of MWCNT/PEEK and MWCNT-COOH/PEEK-OH composite films compared to PEEK powder indicates that carbon nanotubes play a dominant role in providing nucleation sites for the crystallization of the PEEK resin matrix. Meanwhile, the crystallinity of MWCNT/PEEK and MWCNT-COOH/PEEK-OH composite films is almost the same, indicating that the distribution structure between carbon nanotubes and resin in both composite films is almost consistent, which can also be seen from the micromorphology of the composite films. Therefore, the composite films prepared by this method can make the MWCNT and PEEK powder uniformly dispersed with each other and significantly improve the crystallinity of PEEK.

Figure 13 (a) shows the tensile test results of MWCNT/PEEK and MWCNT-COOH/PEEK-OH composite films. The tensile strength and elastic modulus of MWCNT-COOH/PEEK-OH composite films are 10.7 MPa and 465.9 MPa, which are significantly higher than those of MWCNT/PEEK composite films at 5.5 MPa and 404.2 MPa, respectively. Because of the presence of -COOH and -OH functional groups within MWCNT-COOH/PEEK-OH composite films, strong hydrogen bonds, and π-π interactions are formed between them, which can significantly improve the interfacial bonding performance [17, 53]. The results of the molecular dynamics also indicate a closer bond between MWCNT-COOH and PEEK-OH and a higher bonding energy. In addition, an esterification reaction between -COOH and -OH may also have occurred during the preparation of the composite films, producing a little ester bonding. Therefore, a stronger force is required to overcome the energy generated by chemical bonding, hydrogen bonding, and π-π interactions within the MWCNT-COOH/PEEK-OH composite film during tension. Figure 13 (b) compares the tensile strength of CNTs/PEEK composites with different CNTs contents. In the previous work, CNTs are mainly doped into PEEK resin using the injection-molding method. Due to the high
viscosity of PEEK resin, the CNTs content is generally 15 wt.% maximum. In the range of 0 ~ 15 wt.%, the tensile strength of CNTs/PEEK composites is enhanced with increasing CNTs content. This work can increase the CNTs content up to 50 wt.% using VSF and hot-pressing methods, but its tensile strength is low. Because of the low content of PEEK in the composite film, PEEK powders cannot fully evenly disperse in the layer. Therefore, after hot pressing, there are still regions connected only by MWCNT inside the composite film. The mechanical properties of these regions are related to the degree of bonding between MWCNT. The tensile strength of this work is clearly higher than that of pure BP, which is also prepared by the VSF method [52]. Furthermore, one future application goal for the MWCNT/PEEK composite films prepared in this work is to enhance the interlaminar mechanical performance of CF/PEEK composites made by the AFP technique. There is already a resin-rich region in the plies, so the MWCNT/PEEK composite films should have less resin content to avoid introducing more resin.

4 Conclusions

In this paper, an MWCNT/PEEK composites film with high carbon nanotube content is envisaged, which will be used as a reinforcing material for CF/PEEK high-performance thermoplastic composites interlaminar resin-rich region. The preparation method of the proposed composite film can solve the problem that the traditional method cannot infiltrate the high-viscosity PEEK into the BP. CNTs are seen to significantly improve the crystallinity of PEEK resin. In addition, molecular dynamics simulation reveals that the chemically modified MWCNT and PEEK are more closely packed and have a better interfacial bonding performance. Finally, it is verified by experiments that the chemically modified MWCNT-COOH/PEEK-OH composite film has a dense structure. Compared with MWCNT/PEEK composite films, the tensile strength and elastic modulus of MWCNT-COOH/PEEK-OH composite films increase by 94.5% and 15.3%, respectively.

Declarations

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CRediT authorship contribution statement

Ziang Jin and Shouzheng Sun are the co-first authors as they contribute equal to this work. Ziang Jin: Methodology, Investigation, Experiment, Writing–Original Draft Preparation. Shouzheng Sun: Methodology, Funding acquisition, Writing–Review & Editing. Sunil Chandrakant Joshi: Review & Editing.
Disclosure statement

No potential conflict of interest was reported by the author(s).

References


Figures

![Microscopic interface model](image_url)

**Figure 1**

Microscopic interface model: (a) MWCNT/PEEK; (b) MWCNT-COOH/PEEK-OH (Red: oxygen atoms, black: carbon atoms, white: hydrogen atoms).
Figure 2

Results of interface microstructure of MWCNT/PEEK and MWCNT-COOH/PEEK-OH models: (a) RDF; (b1) RC-X; (b2) RC-Y; (c1) MSD; (c2) Diffusion coefficient; (d) FFV.
Figure 3

The interfacial adsorption energy of MWCNT/PEEK and MWCNT-COOH/PEEK-OH models
Figure 4

Schematic diagram of MWCNT/PEEK composite film preparation process.
Figure 5

Micromorphology of the chemically modified and unmodified powder: (a) MWCNT; (b) MWCNT-COOH; (c) PEEK; (d) PEEK-OH.
Figure 6

Micromorphology of the preformed films: (a) Surface of MWCNT/PEEK; (b) Surface of MWCNT-COOH/PEEK-OH; (c) Cross section of MWCNT/PEEK; (d) Cross section of MWCNT-COOH/PEEK-OH.
Figure 7

Micromorphology of the composites films: (a) Surface of MWCNT/PEEK; (b) Surface of MWCNT-COOH/PEEK-OH; (c) Cross section of MWCNT/PEEK; (d) Cross section of MWCNT-COOH/PEEK-OH.
Figure 8

N2 adsorption isotherm: (a) MWCNT/PEEK composite films; (b) MWCNT-COOH/PEEK-OH composite films.

Figure 9

XPS and FTIR diffraction curves: (a) C1 spectra of MWCNT powder; (b) C1 spectra of MWCNT-COOH powder; (c) FTIR spectra of MWCNT and MWCNT-COOH powder.
Figure 10

XPS and FTIR diffraction curves: (a) C1 spectra of PEEK powder; (b) C1 spectra of PEEK-OH powder; (c) O1 spectra of PEEK powder; (d) O1 spectra of PEEK-OH powder; (e) FTIR spectra of PEEK and PEEK-OH powder.
Figure 11

XPS and FTIR diffraction curves: (a) C1 spectra of MWCNT/PEEK composite film; (b) C1 spectra of MWCNT-COOH/PEEK-OH composite film; (c) FTIR spectra of MWCNT/PEEK and MWCNT-COOH/PEEK-OH composite film; (d) O1 spectra of MWCNT-COOH/PEEK-OH composite film.
Figure 12

XRD diffraction curve and peak fitting: (a) XRD diffraction curve of MWCNT, PEEK, MWCNT/PEEK, and MWCNT-COOH/PEEK-OH; (b) XRD peak fitting of PEEK; (c) XRD peak fitting of MWCNT/PEEK; (d) XRD peak fitting of MWCNT-COOH/PEEK-OH.
Figure 13

Tensile strength and elastic modulus: (a) MWCNT/PEEK and MWCNT-COOH/PEEK-OH composite films; (b) Comparison of different CNTs content [47-52].

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