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Optimization of Process Parameters and Microscopic Morphology of Multi-Walled Carbon Nanotubes/PEEK Films Using the Vacuum Suction Filtration Method

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Abstract: Multi-walled carbon nanotubes (MWCNTs) are a high-quality interlamination reinforcement material, but the high viscosity of polyetheretherketone (PEEK) prevents good fusion between MWCNTs and PEEK. This study proposes a method to achieve the complete integration of MWCNTs and PEEK through the preparation of a composite film using the vacuum suction filtration (VSF) method and optimizes the process parameters. An orthogonal experiment with three factors (filter paper pore size, ultrasonic dispersion time, and PEEK content) at three levels is designed, and mechanical performance testing and microscopic morphology observation are conducted. The influence of the three factors of filter paper pore size, ultrasonic time, and PEEK content on the elastic modulus and tensile strength of the film is investigated. The results are a filter paper pore size of 0.45 μm , ultrasonic time of 8.3 h, and PEEK content of 336.524 mg. The mechanical performance obtained under the optimal process parameters are an elastic modulus of 2437.5723 MPa and a tensile strength of 46.5196 MPa. This optimal process increases the elastic modulus by 12.3152% while maintaining a high tensile strength.



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Keywords: mechanical performance; microstructure; process parameter optimization; MWCNTs/PEEK composite film

1. Introduction

Polyether-ether-ketone (PEEK) is a commonly used high-performance thermoplastic resin. It possesses numerous advantages, including exceptional toughness and damage resistance, excellent environmental resistance, good creep and fatigue resistance, as well as outstanding wear resistance [1,2]. PEEK exhibits excellent mechanical performance, conductivity, and chemical resistance [3]. Recent research in the field of interlamination reinforcement has primarily focused on incorporating reinforcing agents such as nanoparticles, nanofibers, and films into the matrix [4,5]. Multi-walled carbon nanotubes (MWCNTs) are considered high-quality interlamination additives due to their large aspect ratio, high surface area, superior mechanical performance, and high modulus. MWCNTs possess an exceptionally high specific surface area, as well as outstanding mechanical strength and modulus. When dispersed within a PEEK matrix, they can significantly enhance the tensile strength and elastic modulus of the material. This is attributed to the ability of MWCNTs to withstand greater forces when subjected to external loading, thereby resisting deformation and fracture. Additionally, the grid structure of MWCNT films facilitates easier infiltration by resins, thereby enabling a tight “bridging” between layers in composite materials. In the event of PEEK damage, MWCNTs impede the propagation of microcracks, effectively delaying the fracture process of PEEK. Moreover, when the matrix undergoes damage, MWCNTs are pulled out from it, absorbing energy and leading to a “pinning” effect, thus enhancing

the mechanical performance of the film. Figure 1 shows the enhancement mechanism of MWCNTs for substrates. At the microscale, both PEEK and MWCNTs contain surface oxygen-containing functional groups, leading to chemical reactions and the formation of π - π bonds. This enhances intermolecular interface interactions, thereby strengthening their mechanical properties.

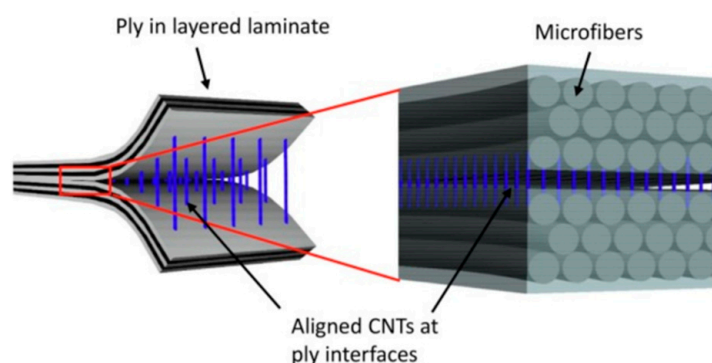


Figure 1. The principle of enhancing resin-based composite materials with MWCNTs [6].

In the past few decades, there has been a continuous pursuit of achieving uniform dispersion of MWCNTs in PEEK to enhance the performance of composite films. Directly using MWCNTs as the reinforcing phase can lead to their agglomeration due to their high specific surface area, particularly under the influence of van der Waals forces [7,8]. This results in uneven internal dispersion when incorporated into PEEK resin with higher viscosity [9]. The use of carbon nanosheets can result in an excessive content of MWCNTs, preventing sufficient infiltration of PEEK into the inner regions of the carbon nanosheets. To prepare high-performance composite films, it is essential to achieve a uniform dispersion of MWCNTs within PEEK, thus serving as an effective reinforcing phase [10,11]. The key to determining whether the composite film can serve as a good reinforcing phase lies in ensuring good dispersion of PEEK powder and MWCNTs within the film. Two commonly used methods for preparing composite films are vacuum suction filtration and chemical vapor deposition [12]. Composite films prepared by chemical vapor deposition have a higher density, making it difficult for them to fuse with the resin matrix as a reinforcing phase. Vacuum suction filtration (VSF) allows for the adjustment of film uniformity and density by modifying parameters, and the resulting films are relatively loose, making them suitable as reinforcing phases [13,14]. VSF is better for controlling the PEEK content of films. However, there is limited research on process parameter optimization in this regard. In previous studies, the focus of MWCNTs/PEEK films is mainly on additives and changing the chemical surface modifications of MWCNTs, and only a small portion of the papers propose specific fabrication processes for the films [15–17]. This paper proposes a new process for preparing the film, which ensures the molding rate and molding quality of the film. It is an innovative method by considering the influence of process parameters on the mechanical properties of films during the preparation process of MWCNTs/PEEK films. The use of solvent-assisted dispersion has proven to be a viable method for dispersing MWCNTs [15]. Nevertheless, due to the unique chemical performance and higher melting temperature of PEEK, the choice of suitable solvents for assistance becomes limited. Changing the chemical functional groups can improve the interfacial interaction between PEEK and MWCNTs. This change, therefore, may adversely affect the mechanical properties of MWCNTs due to the change in chemical composition. MWCNTs, owing to their distinctive physical and chemical properties, are recognized as an excellent material for interlaminar reinforcement. Direct integration into composite matrices often leads to heterogeneous distribution of MWCNTs; conversely, film fabrication techniques enable the uniform fixation of MWCNTs within the film structure. Introducing MWCNTs/PEEK composite films as an interlaminar reinforcing phase substantially enhances the mechanical performance of composite materials [18].

In this paper, a new preparation process is used to prepare composite films by using the VSF method, which can effectively control the process parameters during the preparation process. The mechanical properties of the films are improved and the dispersion of carbon nanotubes in the films is optimized by adjusting the process parameters [19,20]. The second part of the paper describes the materials and preparation methods. The third part is mechanical performance testing and micro-morphology analysis. The fourth part is the optimization of process parameters [21].

2. Materials and Methods

2.1. Preparation of MWCNTs/PEEK Composite Films

2.1.1. Materials

This experimental preparation process will use the following materials: 1. MWCNTs are purchased from Jiakai Technology Co., Ltd. (from Chengdu, China), with a powder diameter of 10–30 nm, a length of 10–30 μm , and a specific surface area of 150–200 m^2/g . 2. PEEK powder is purchased from Qiangsheng Plasticizing Raw Materials Co., Ltd. (from Wenzhou, China). 3. The surfactant Triton (X-100) is purchased from China Medicine and Chemical Reagent Co., Ltd. (Shanghai, China). The density of the reagent is 0.98 g/mL, the fog point is 75 °C–85 °C, and the concentration is 10%. It is used to improve the hydrophobicity of PEEK powder and MWCNTs. 4. The filter membrane is purchased from Haining New Material Technology Co., Ltd. (from Haining, China), with three specifications of average pore size: 0.22 μm , 0.45 μm , and 0.8 μm .

2.1.2. Preparation Processes

1. In the Lechen precision electronic balance, 60 mg of MWCNT powder and different mass ratios of PEEK powder are precisely weighed and placed into a beaker. Subsequently, 500 mL of deionized water and a surfactant comprising 10% of the combined powder mass are added.

2. The two solutions are then mechanically stirred for 30 min, after which they are subjected to ultrasonic dispersion once the surface foam has been eliminated.

3. An additional 400 mL solution of PEEK powder is prepared, with the PEEK powder accounting for 50% of the total mass of the mixed powder. This solution is used as a base during vacuum filtration.

4. The above two cups of solutions are dispersed ultrasonically for the experimentally predetermined time. In order to prevent the two cups from becoming too hot, the cooling water needs to be changed every half an hour.

5. Once the ultrasonic dispersion is completed according to the predetermined time, two cups of solution are obtained. The filtration device is then removed and rinsed thoroughly with deionized water, after which 150 mL of the PEEK powder solution is poured into the filtration device as the base layer for the composite membrane.

6. The mixed solution containing MWCNT powder and PEEK powder is poured into the filtration device, with careful attention to avoid any precipitation entering the device.

7. The filter paper containing the composite membrane is then removed from the device and dried. After drying, the composite membrane is placed into a hot-press machine and held at 1.3 MPa and 360° for ten minutes. Finally, the composite membrane is allowed to cool naturally to room temperature while maintaining pressure.

The specific operation flow is shown in Figure 2 below.

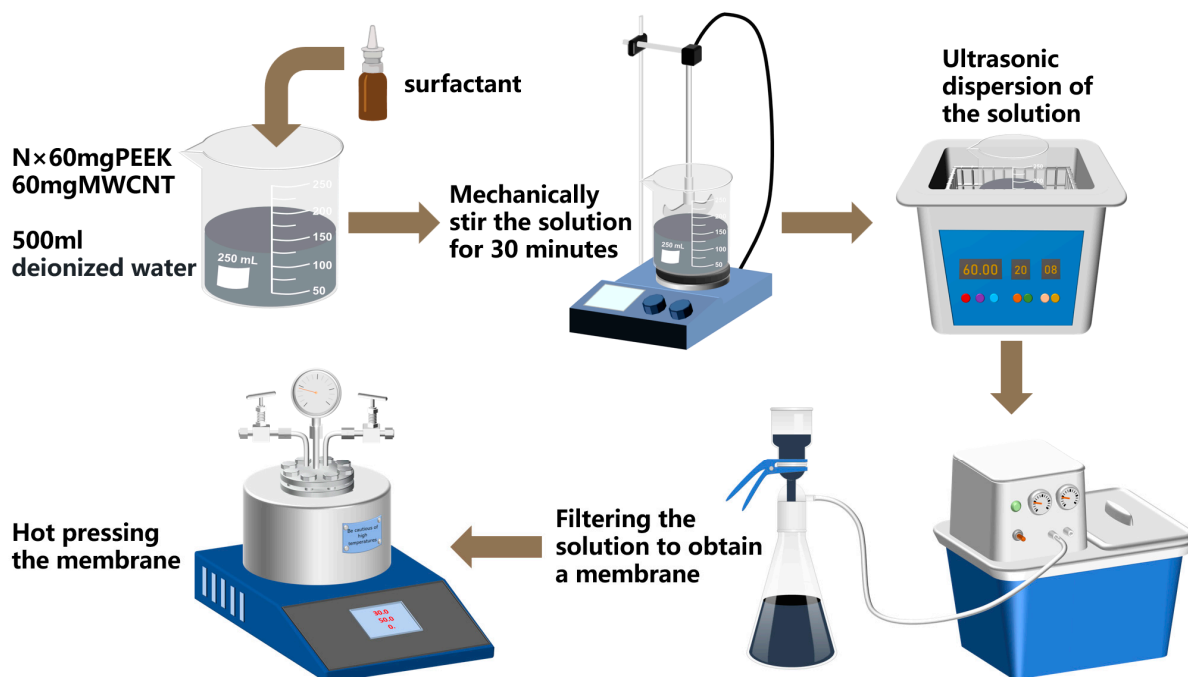


Figure 2. The process of MWCNTs/PEEK film fabrication.

2.2. Performance Characterization Methods

The performance characterization of MWCNTs/PEEK film is carried out using two methods: mechanical tensile performance testing and microscopic observation of the microstructure. The mechanical tensile performance testing utilized the Shenzhen Sansi tensile tester UTM4103, with a load sensor specification of 20 N and a loading speed of 1 mm/min. The interfacial shear strength is tested according to the national standard GB/T 1449-2005 [22]. Three mechanical performance indicators were selected: tensile strength, elastic modulus, and fracture elongation. After testing, the fractured samples were preserved for the subsequent microscopic interface analysis.

Prior to the microscopic observation of the sample surface, gold coating was applied due to the sample's non-conductivity. The gold coating was performed using the American Gatan682 (USA) precision etching and sputtering system, with ion beam energy of 110 keV, tilt angle of 90°, tilt speed of 40°/s, and rotation speed of 1060 rpm. The sample is sputter-coated with gold to a thickness of 10 nanometers. Following the gold coating, the samples were observed using the American FEI company's (USA) HELIOS Nano Lab 600i scanning electron microscope (SEM) to characterize the microstructure of the samples.

3. Microscopic Morphology and Mechanical Performance of MWCNTs/PEEK Composite Films

3.1. Mechanical Performance of MWCNTs/PEEK Composite Films

Owing to the multiplicity of variables that influence the film formation process, the application of a full factorial experimental design to effectively assess the impact of various factors on film properties is rendered impracticable within a finite number of experimental iterations, resulting in an excessive duration for the experimental phase. Consequently, this investigation prioritizes three critical processing parameters, each of which exerts a substantial influence on the film's performance.

The initial parameter of interest is the PEEK content within the composite film. The proportion of PEEK not only governs the success of the film formation process but also significantly affects the distribution of MWCNTs within the film matrix. An overabundance of PEEK impedes the reinforcing potential of MWCNTs, whereas an insufficient quantity may catalyze the agglomeration of the nanotubes—both scenarios detracting from the film's desired properties.

The second parameter under consideration is the ultrasonic dispersion duration, a critical factor that determines the homogeneity of the MWCNTs/PEEK mixture. Optimal dispersion, achieved during the ultrasonic treatment, is integral to attaining a film of superior quality.

Lastly, the investigation contemplates the pore size of the filtration paper. This parameter plays a pivotal role by dictating the particle size of the MWCNTs/PEEK composite during the filtration process, thereby directly influencing the resultant film quality.

A three-factor, three-level orthogonal experiment will be conducted to evaluate the film performance and optimize the parameters. Several sets of composite films with different process parameters will be prepared for the orthogonal experiment, with the parameter ranges determined based on the literature [23]. The selected experimental parameters are shown in Table 1. The three selected variables are filter paper pore size, ultrasonic time, and the mass ratio of MWCNTs to PEEK powder. The orthogonal experiment will determine the comprehensive influence of the selected process parameters on the measured mechanical performance. The composite films will be cut into rectangular specimens measuring 50 mm in length and 10 mm in width, and then mechanical tensile testing will be conducted. Figure 3 shows the mechanical testing machine.

Table 1. The orthogonal experimental table.

Group	Pore Size of Filter Paper	Time	Mass Ratio
1	0.45 μm	3 h	1:1
2	0.45 μm	6 h	1:8
3	0.45 μm	9 h	1:4
4	0.8 μm	3 h	1:8
5	0.8 μm	6 h	1:4
6	0.8 μm	9 h	1:1
7	1.2 μm	3 h	1:4
8	1.2 μm	6 h	1:1
9	1.2 μm	9 h	1:8

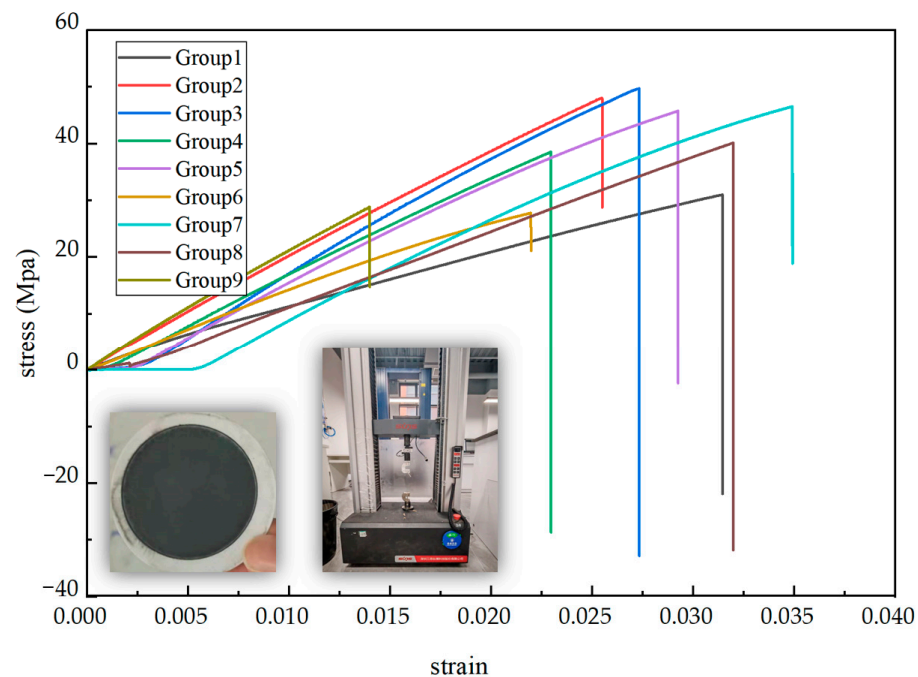


Figure 3. The stress–strain curve of MWCNTs/PEEK film.

Combining Tables 1 and 2 and Figures 3 and 4, the following can be roughly concluded:
1: When the mass ratio of MWCNTs to PEEK is 1:4 or 1:8, the mechanical performance is

significantly better than at a ratio of 1:1. 2: Ultrasonic dispersion time also has a serious impact on the mechanical performance of the film, with shorter ultrasonic times resulting in less stable quality. For the same mass ratio of MWCNTs to PEEK powder, ultrasonic time affects the mechanical performance of the film. 3: The optimal mass ratio of MWCNTs to PEEK powder is around 1:4, generally slightly higher than 1:8. This is likely due to better parameters of the carbon nanotubes in the former, which can help fuse the MWCNTs and PEEK powder more effectively, while the latter has too much resin, which prevents the carbon nanotubes from strengthening the resin matrix. 4: The smaller the pore size of the filter paper, the lower the average thickness and elongation at break of the film, which may affect its toughness. Figure 4 shows the mechanical performance test of the experimental specimens, indicating that the tested MWCNTs/PEEK film has good mechanical performance, exhibiting good stiffness and strength when subjected to external forces. The high specific surface area and nano-effect of the carbon nanofilm contribute to enhancing the interaction between it and thermoplastic materials. This interaction can be achieved through chemical bonding, physical adsorption, and other means, further improving the interlamination bonding strength. This enhanced interaction also helps prevent interlamination crack propagation, improving the material's fatigue resistance and impact resistance. Most of the tensile fracture displacements of the composite films are around 0.6 mm, and the tensile forces at fracture are between 40 and 70 MPa. This figure reflects the overall mechanical performance of the MWCNTs/PEEK composite film.

Table 2. Mechanical performance testing results.

Group	Tensile Strength	Elastic Modulus	Elongation at Break
1	31.0181 MPa	952.6326 MPa	3.14
2	61.944 MPa	2128.4348 MPa	4.22
3	43.4245 MPa	2136.6987 MPa	2.32
4	38.5375 MPa	1848.165 MPa	2.30
5	45.7498 MPa	1913.6859 MPa	2.92
6	27.7818 MPa	1484.7015 MPa	2.20
7	37.544 MPa	2162.805 MPa	3.49
8	28.5746 MPa	1300.84915 MPa	3.05
9	28.8517 MPa	2005.1019 MPa	1.40

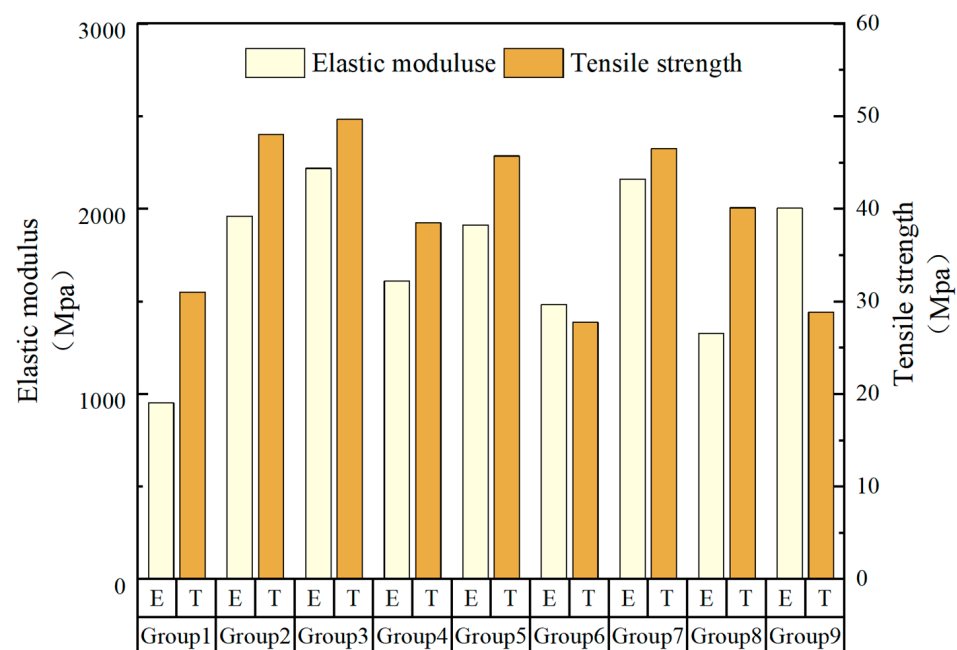


Figure 4. MWCNTs/PEEK film mechanical performance bar chart.

3.2. Microscopic Morphology of the MWCNTs/PEEK Film

After mechanical performance testing of the specimens in the previous step, the fracture surface of the samples was observed under a scanning electron microscope (SEM) for microscopic morphology analysis.

The above images depict the microscopic morphology of composite films with different process parameters under a scanning electron microscope. Figure 5a shows the microscopic morphology when the mass ratio of MWCNTs to PEEK powder is 1:1. At this ratio, due to the excessive content of MWCNTs, aggregation of carbon nanotubes occurs under the influence of electrostatic and van der Waals forces, resulting in poor embedding within the PEEK matrix. The high content of MWCNTs leads to the predominance of van der Waals forces between MWCNTs molecules over the bonding forces between MWCNTs and PEEK molecules, significantly impairing the mechanical performance of the composite film. Hence, this process parameter is not optimal. Figure 5b shows the microscopic morphology when the mass ratio of MWCNTs to PEEK powder is 1:4. At this ratio, MWCNTs are uniformly distributed around the PEEK matrix, effectively inhibiting the propagation of small cracks upon the rupture of the composite film, preventing the enlargement of cracks that lead to film failure. Additionally, MWCNTs can be pulled out upon matrix rupture, absorbing energy and exhibiting a “pinning” effect, thereby enhancing the overall mechanical performance of the composite film. The incorporation of MWCNTs can establish a network structure within the PEEK matrix capable of dissipating energy. When the material is subjected to impact or deformation, MWCNTs can facilitate mechanisms such as crack deflection, branching, and bridging, thereby enhancing the material’s fracture toughness. Figure 5c depicts the microscopic morphology when the mass ratio of MWCNTs to PEEK powder is 1:8. At this ratio, due to an excess of the resin matrix, carbon nanotubes are fully surrounded, with only a minimal portion protruding on the fracture surface, and no apparent pull-out phenomenon is observed. The MWCNTs at this process parameter do not effectively enhance the film upon rupture, resulting in slightly lower average mechanical performance compared to the 1:4 ratio parameters.

The two images above depict the cross-sectional microscopic morphology of composite films with varying ratios of MWCNTs to PEEK. These images illustrate the impact of different mass ratios on the cross-section. Figure 6a corresponds to a mass ratio of MWCNTs to PEEK powder of 1:4. Figure 6a elucidates the reinforcement mechanism of MWCNTs within the PEEK matrix. It is apparent from Figure 6a that the fracture surface of the resin matrix exhibits numerous uneven regions in the presence of an increased concentration of MWCNTs. The topography of these uneven areas contrasts markedly with the smooth fracture morphology associated with high PEEK content. This disparity is attributable to the disruption caused by MWCNTs during fracture. It illustrates that MWCNTs effectively enhance the PEEK matrix by mechanisms such as crack deflection, crack bridging, and the mitigation of stress concentrations. Figure 6b represents a mass ratio of MWCNTs to PEEK powder of 1:8. In this scenario, the cross-section appears remarkably smooth, with minimal protrusion of carbon nanotubes on the surface. This indicates that at this ratio, the high content of PEEK almost entirely encapsulates the carbon nanotubes, failing to enhance the film upon fracture.

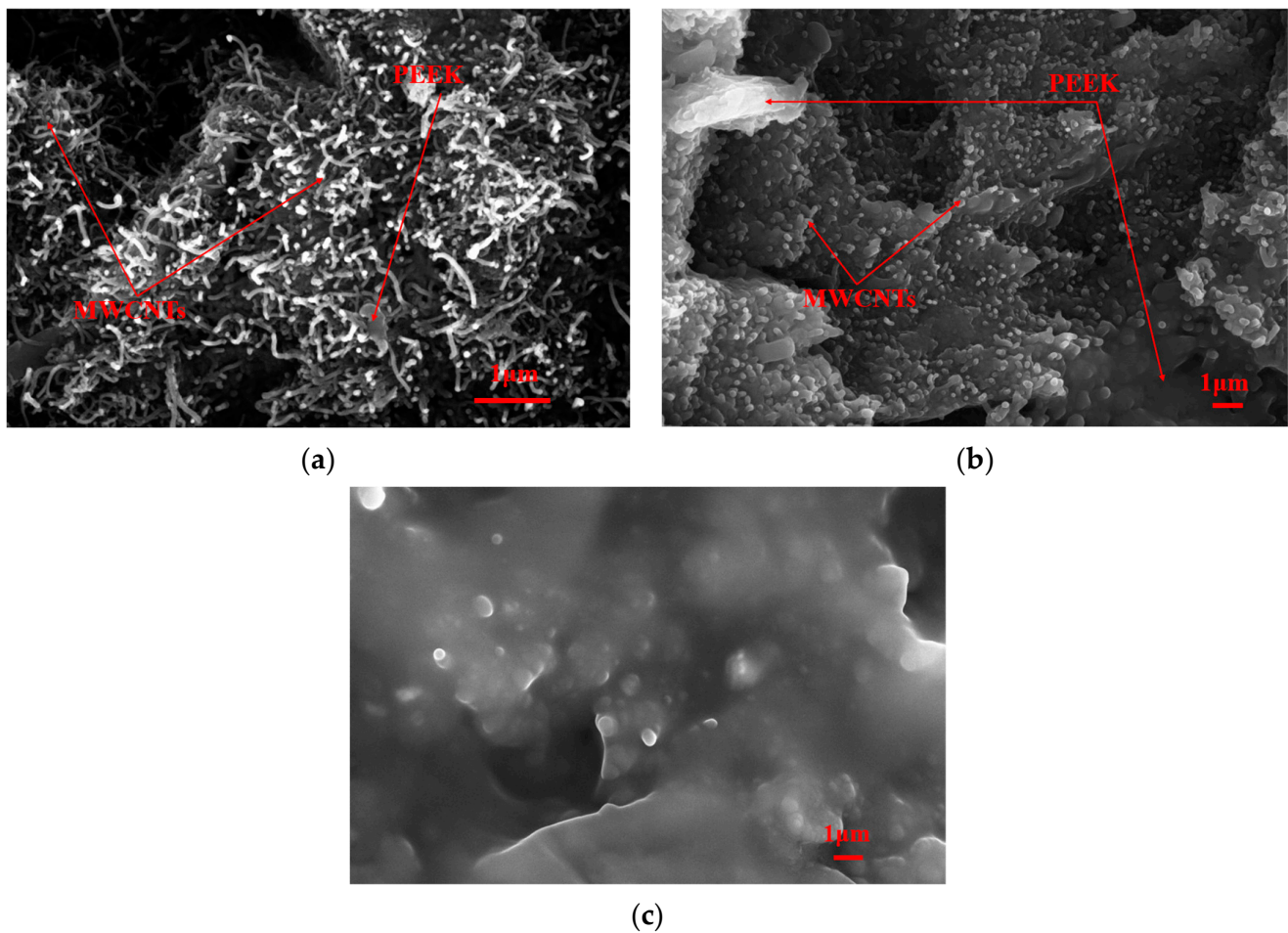


Figure 5. Microstructure of films with different PEEK contents at the fracture site: (a) The figure shows the 1:1 ratio of MWCNTs to PEEK. (b) The figure shows the 1:4 ratio of MWCNTs to PEEK. (c) The figure shows the 1:8 ratio of MWCNTs to PEEK.

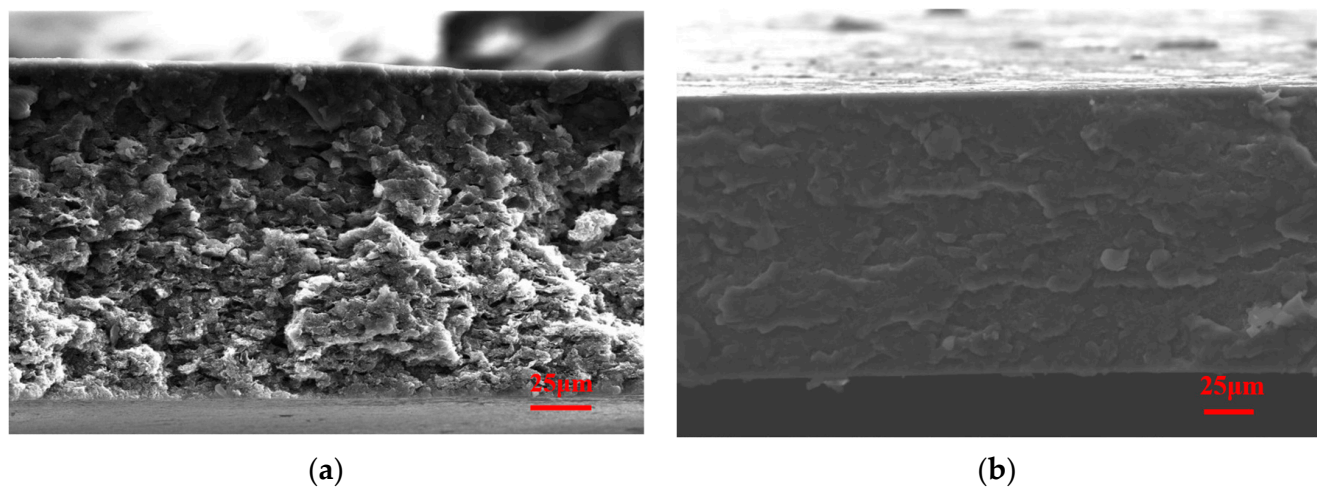


Figure 6. Microscopic morphology of cross-sections with different PEEK contents. (a) The figure shows the surface micro-morphology when the PEEK content is low. (b) The figure shows the surface micro-morphology when the PEEK content is high.

The above two images depict the microscopic morphology of composite films with ultrasonic dispersion times of 3 h and 9 h, respectively. Figure 7a illustrates the microdispersion of MWCNTs in a composite film subjected to 3 h of ultrasonic agitation. It is evident that short-duration ultrasonic dispersion results in inadequate dispersion of MWCNTs within the resin matrix of the film. While suitable mass ratios prevent extensive van der Waals aggregation of MWCNTs, allowing for effective encapsulation of MWCNTs by the PEEK matrix, the distribution within the matrix remains uneven. Consequently, uneven absorption of energy occurs upon MWCNT extraction, leading to insufficient reinforcement of certain regions of the matrix due to lower MWCNT content. Insufficient dispersion time results in uneven mechanical performance across different regions, which is detrimental to the overall mechanical performance of the film. Figure 7b portrays the surface morphology after 9 h of ultrasonic dispersion. It is evident that with sufficient ultrasonic time, carbon nanotubes are uniformly distributed between PEEK matrices, effectively reinforcing the PEEK matrix. Observations of the specified image alongside complementary scanning electron microscopy (SEM) images have facilitated the calculation of MWCNT densities within the film. For distributions characterized by extended ultrasonic times, uniformity is achieved, with the density ranging from 5.02 to 7.10 MWCNTs per square micrometer. Conversely, shorter ultrasonic treatments result in less uniform distributions, where areas of aggregations present densities of 40 MWCNTs per square micrometer, and zones featuring sparse distributions exhibit negligible MWCNT presence. These calculated observations distinctly corroborate that ultrasonic time is a pivotal factor influencing the molding process of MWCNTs/PEEK films. This factor is instrumental in determining the uniformity of MWCNT dispersion throughout the film, thereby directly affecting its mechanical performance.

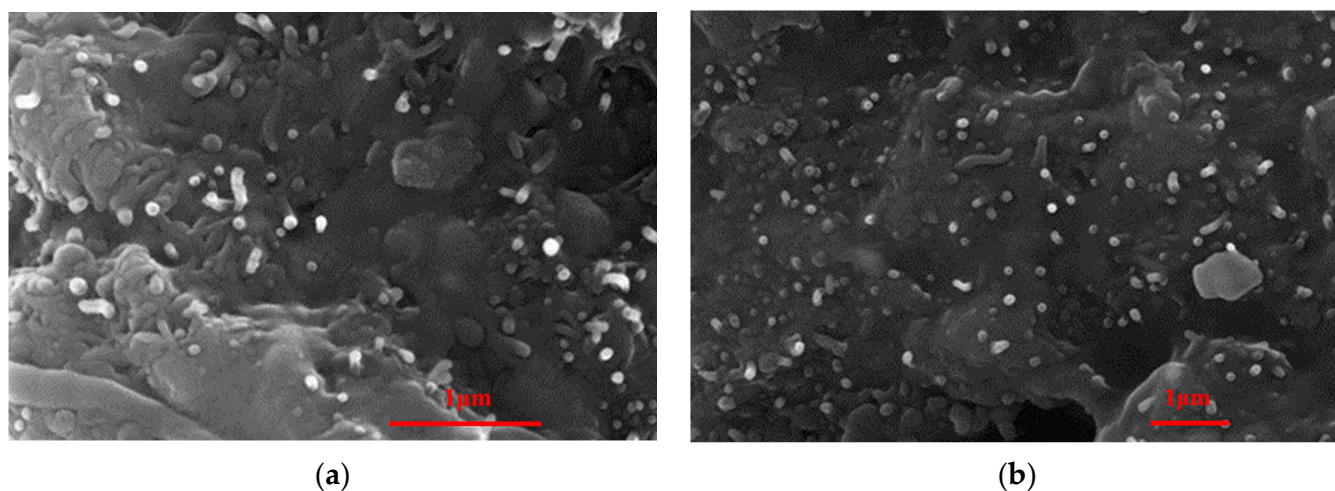


Figure 7. The microscopic morphology inside films with different ultrasonic times: (a) The figure shows an ultrasonic dispersion time of 3 h. (b) The figure shows an ultrasonic dispersion time of 9 h.

4. Response Surface Methodology to Optimize Optimal Parameters

4.1. Analysis of the Fitted Model

The response surface methodology is a statistical modeling technique used to study and optimize the relationship between factors or variables that influence a specific response variable. It is commonly employed in engineering, science, experimental design, and other fields to analyze and optimize complex systems or processes. This chapter applies the response surface methodology to fit a multivariate regression equation between the response factors and response values, aiming to explore optimal process parameters through analyzing response surface contour lines. Based on the orthogonal experiments in Chapters Two and Three, this performance conducts research on filter paper pore size, ultrasonic time, and the mass ratio of MWCNTs to PEEK powder using the response surface method. Three fitting models for the mechanical performance of MWCNTs/PEEK composite films

are obtained: linear model, two-factor model, and quadratic model. The fitting results are illustrated in the following figure.

By observing Tables 3 and 4, the following information can be obtained. For both the elastic modulus and tensile strength models, the significance p -values of the quadratic model are all less than 0.0001, indicating a strong correlation between the response factors and the response values. The negative Predicted R2 implies that the model consistently predicts the response variable better. Adeq Precision, a metric for evaluating experimental models, reflects the signal-to-noise ratio, where the signal refers to the impact of experimental factors on the response variable, and noise refers to the influence of experimental errors or interfering factors on the experimental results. Generally, an Adeq Precision value greater than 4 indicates a reasonable situation. The Adeq Precision values for the predicted models of the elastic modulus and tensile strength are 630.5786 and 355.1417, respectively. Adeq Precision can also be considered alongside the coefficient of variation (C.V.); a smaller C.V. indicates greater experimental reliability. The C.V. values for the predicted models of the elastic modulus and tensile strength are 0.1279% and 0.1695%, respectively. In conclusion, the quadratic model is selected to fit both parameters. Based on the quadratic equation fitting, the regression equation for the elastic modulus is as follows:

$$T = 1948.5 + 13.5A + 181.9B + 330.7C - 1235.5AB + 43.5AC + 1019.4BC - 921.1A^2 - 37.5B^2 + 661.5C^2$$

Tensile strength is as follows:

$$T = 46.6 - 1.7A - 1.6B + 2.2C + 17AB - 6.8AC - 16.7BC + 20.2A^2 - 0.8B^2 - 29.6C^2$$

In this context, A is the filter paper pore size, B is the ultrasonic time, and C is the content of PEEK. The impact factors on the mechanical performance of MWCNTs/PEEK films are as follows: PEEK content (C) has the greatest influence, followed by ultrasonic time (B), and then filter paper pore size (A). The interactive effects of these factors on the film's mechanical performance are ranked as follows: A-B > B-C > A-C. Therefore, the single factor of PEEK content has the most significant impact on the mechanical performance of the film, while the interactive effect of filter paper pore size and ultrasonic time has the greatest influence.

Table 3. Different models of elastic modulus.

Source	Sequential p -Value	Adjusted R2	Predicted R2
Linear	0.1623	0.2252	−0.8350
2FI	0.0126	0.7865	−1.8202
Quadratic	<0.0001	0.9999	−2.6730

Table 4. Different models of tensile strength.

Source	Sequential p -Value	Adjusted R2	Predicted R2
Linear	0.8646	−0.2336	−2.1906
2FI	0.0515	0.4465	−6.0720
Quadratic	<0.0001	0.9999	−6.5487

4.2. Analysis of Fitting Results

For the quadratic regression equation, the results of the fitting for factors A, B, and C can be derived. The analysis below pertains to the interaction between these three factors on the elastic modulus and tensile strength.

Initially, a strong correlation between the pore size of the filter paper and the ultrasonic time is apparent. Figure 8 illustrates the interactive effects of the filter paper pore size and ultrasonic dispersion time on the elastic modulus when the PEEK quantity is 240 mg. From the figure, one can observe that a shorter ultrasonic duration paired with a smaller

pore size of the filter paper corresponds to a lower elastic modulus. The elastic modulus increases with the enlargement of the filter paper pores. Conversely, for longer ultrasonic treatments, the elastic modulus is higher for smaller pore sizes and decreases as the pore size increases. The diagram below displays the singular effect of the filter paper pore size on the elastic modulus at the specific time intervals of 3 and 9 h of ultrasonication. Figure 8 shows the filter paper pore size and ultrasonic dispersion time interaction effects, while Figure 9 illustrates their single-factor effects.

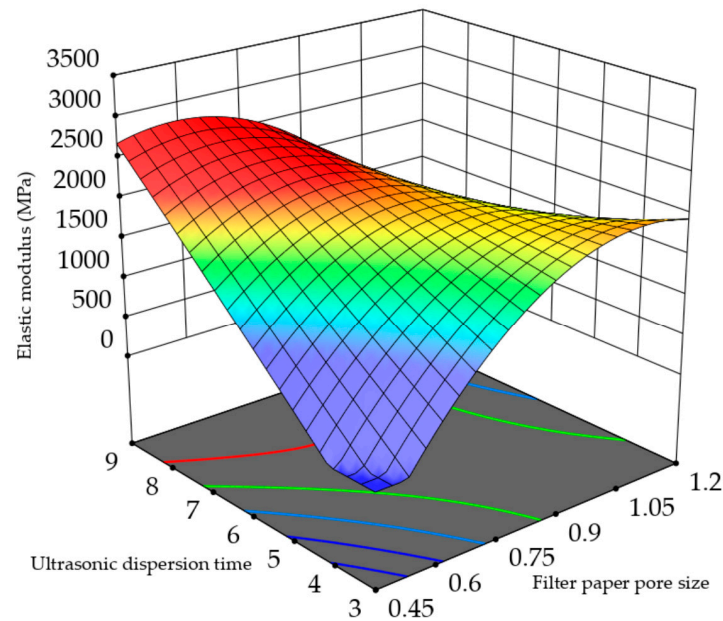


Figure 8. Interaction effect of filter paper pore size and ultrasonic dispersion time on elastic modulus at 240 mg PEEK quantity.

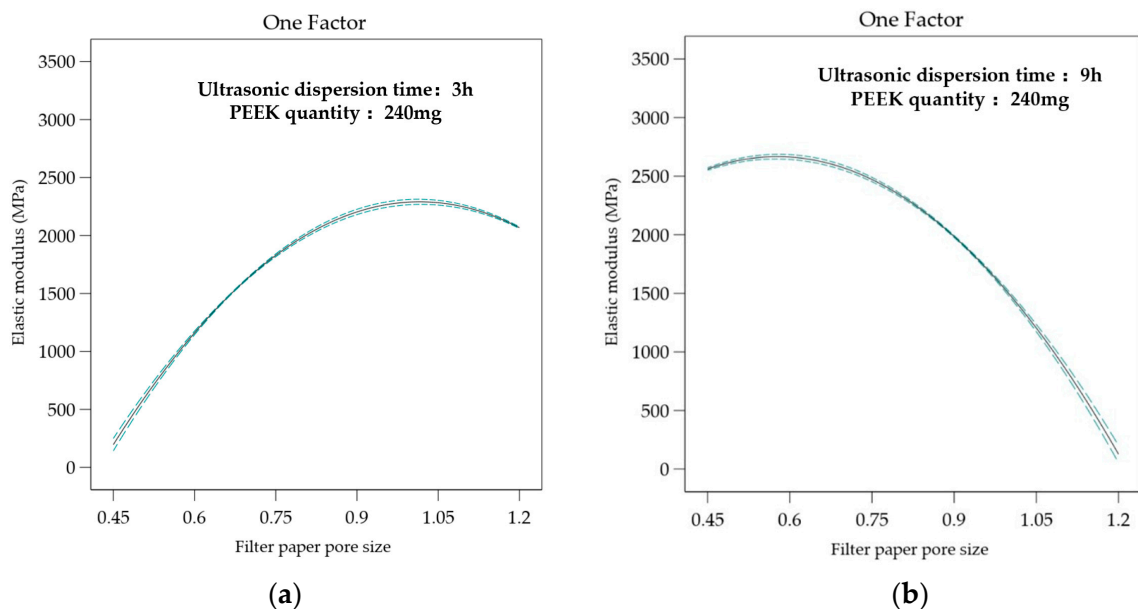


Figure 9. Effect of pore size on elastic modulus for filter paper with PEEK quantity of 240 mg: (a) When the ultrasound dispersion time is 3 h. (b) When the ultrasound dispersion time is 6 h. (The diagram contains solid and dashed lines, where the solid line represents the fitted function, and the interval between the two dashed lines indicates the error range.).

According to the quadratic regression equation, the second most significant interactive factor affecting the elastic modulus is the ultrasonic dispersion time combined with the PEEK quantity. Figure 10 indicates that at a lower PEEK quantity, the elastic modulus decreases with increasing ultrasonic time. Conversely, at higher PEEK contents, the elastic modulus increases with longer ultrasonic durations. The influence of ultrasonic time on the elastic modulus approximately forms a linear trajectory. A higher ultrasonic duration reduces the elastic modulus for lower PEEK quantity, while shorter ultrasonic periods lead to an increased elastic modulus for these contents. Overall, the values of the elastic modulus exhibit a trend of an initial decrease followed by an increase. Figure 10 shows the ultrasonic dispersion time and PEEK quantity interaction effects, while Figure 11 illustrates their single-factor effects.

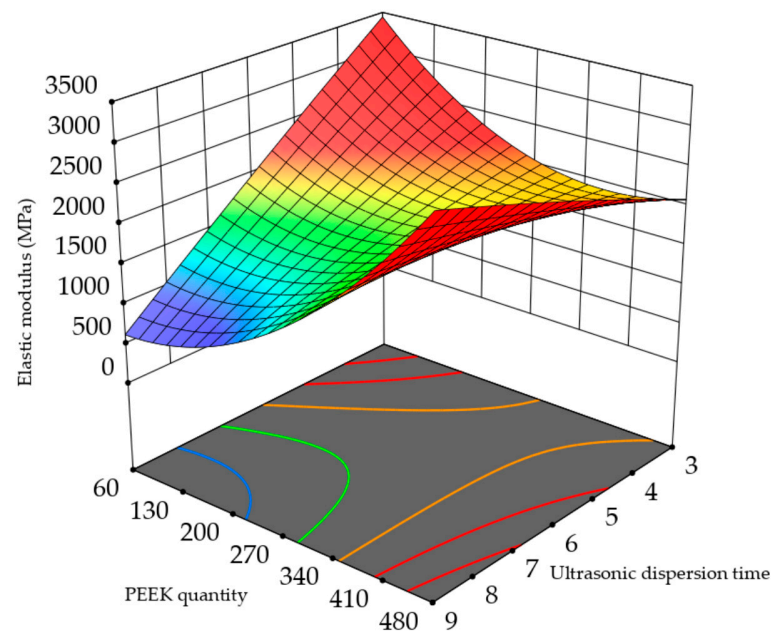


Figure 10. Interaction effect of ultrasonic dispersion time and PEEK quantity on elastic modulus when the pore size of filter paper is 0.8 μm .

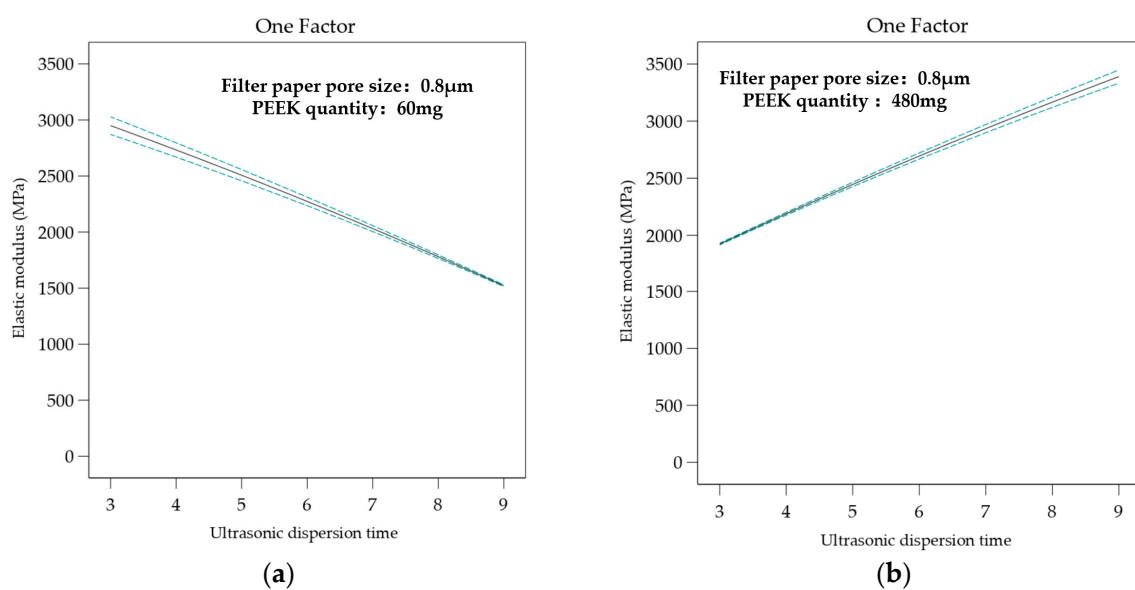


Figure 11. Cont.

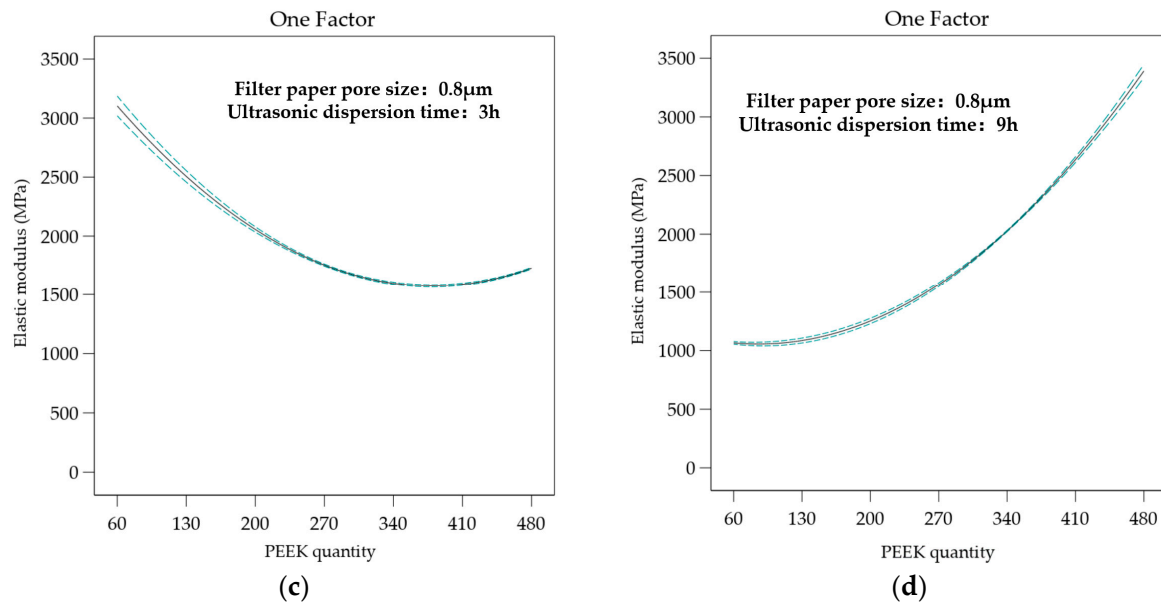


Figure 11. Single-factor effect of ultrasonic dispersion time and PEEK quantity on elastic modulus when filter paper pore size is 0.8 μm . (a) Effect of ultrasonic dispersion time when the quantity of PEEK is 60 mg. (b) Effect of ultrasonic dispersion time when the quantity of PEEK is 480 mg. (c) Effect of PEEK quantity when the ultrasonic dispersion time is 9 h. (d) Effect of PEEK quantity when the ultrasonic dispersion time is 3 h.

The quadratic fitting equation reveals that the A-C interaction, namely the interplay between ultrasonic time and PEEK quantity, has the least impact on the elastic modulus. As observed in Figure 12, when the ultrasonic time is fixed, the influence of the filter paper pore size on the elastic modulus exhibits a trend of initial increase followed by a decrease, regardless of whether the PEEK quantity is high or low. Similarly, regardless of whether the filter paper pore size is large or small, the PEEK quantity first diminishes and then enhances the elastic modulus. The trajectories of both curves essentially alter only the magnitude of the values, with the trends remaining consistent. This observation corroborates the weak influence of the A-C interaction factor on the elastic modulus of the film. Figure 12 shows the filter paper pore size and PEEK quantity interaction effects, while Figure 13 illustrates their single-factor effects.

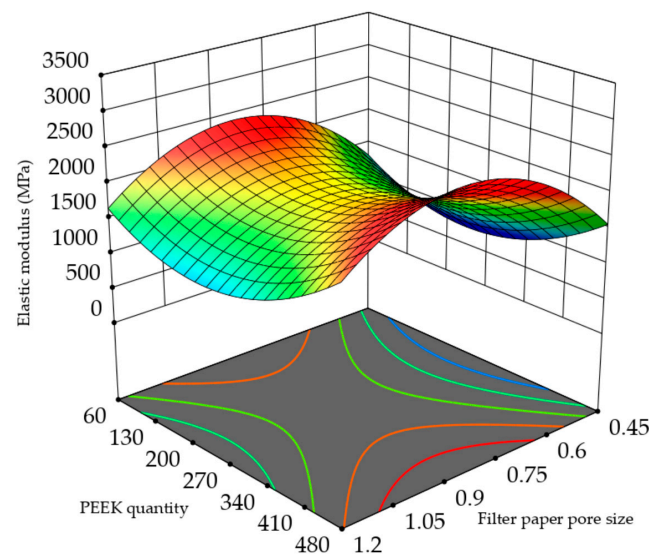


Figure 12. Interaction effect of filter paper pore size and PEEK quantity on elastic modulus when the ultrasonic dispersion time is 6 h.

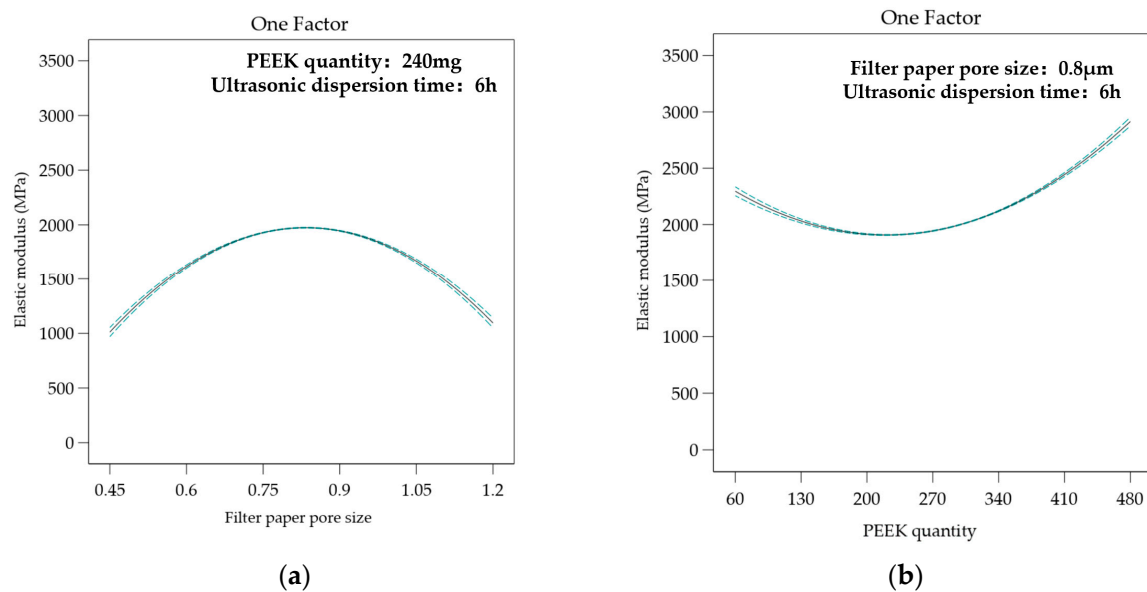


Figure 13. Effect of filter paper pore size and PEEK quantity on elastic modulus when the ultrasonic dispersion time is 6 h. (a) Effect of filter paper pore size when the quantity of PEEK is 240 mg. (b) Effect of PEEK quantity when the filter paper pore size is 0.8 μm .

Figure 14 shows that changes in ultrasonic dispersion time do not significantly change the shape and trend of the curve between filter paper pore size and tensile strength. Overall, patterns exhibit an initial decrease followed by an increase. When the pore size of the filter paper is small, an increase in ultrasonic dispersion time is associated with a decreasing trend in tensile strength. Conversely, for larger pore sizes, an increase in the duration of ultrasonic dispersion corresponds with an increase in tensile strength. The shape of these curves is approximately linear. Figure 14 shows the filter paper pore size and ultrasonic dispersion time interaction effects, while Figure 15 illustrates their single-factor effects.

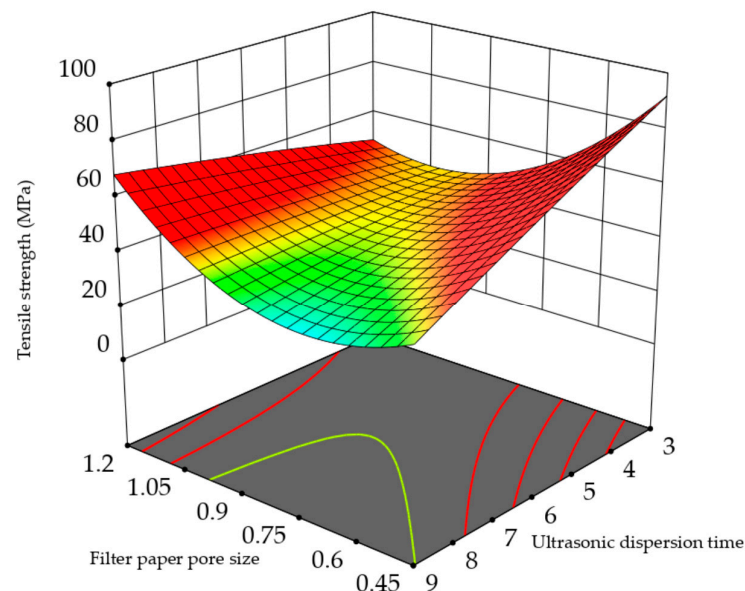


Figure 14. Interaction effect of filter paper pore size and ultrasonic dispersion time on tensile strength when the quantity of PEEK is 240 mg.

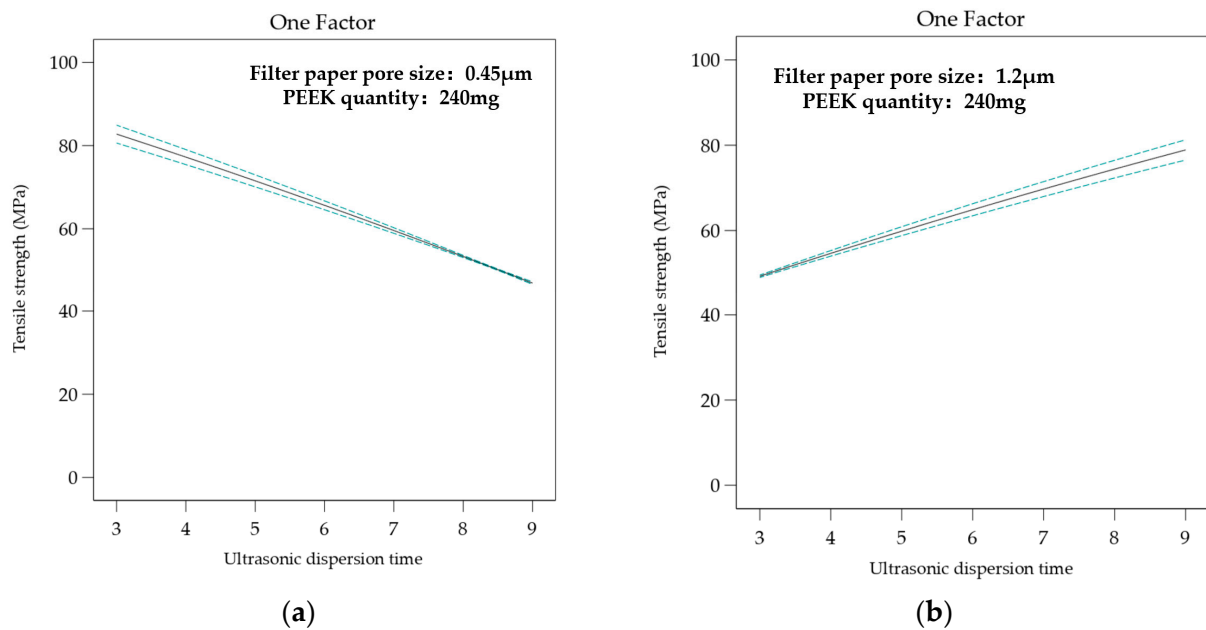


Figure 15. Effect of ultrasonic dispersion time on tensile strength when the quantity of PEEK is 240 mg: (a) Effect of ultrasonic dispersion time when the filter paper pore size is 0.45 μm . (b) Effect of ultrasonic dispersion time when the filter paper pore size is 1.2 μm .

Figure 16 indicates that when the pore size of the filter paper is constant, the ultrasonic dispersion time has a negligible effect on the PEEK quantity. Regardless of the duration of ultrasonic time, the influence curve of PEEK quantity on tensile strength shows a trend of an initial increase followed by a decrease. Meanwhile, the impact trend of ultrasonic time on tensile strength is approximately linear. For a lower PEEK quantity, this trend is characterized by a monotonic increasing linear trajectory. Conversely, for a higher PEEK quantity, the curve tends toward a monotonic decreasing linear trend. Figure 16 shows the PEEK quantity and ultrasonic dispersion time interaction effects, while Figure 17 illustrates their single-factor effects.

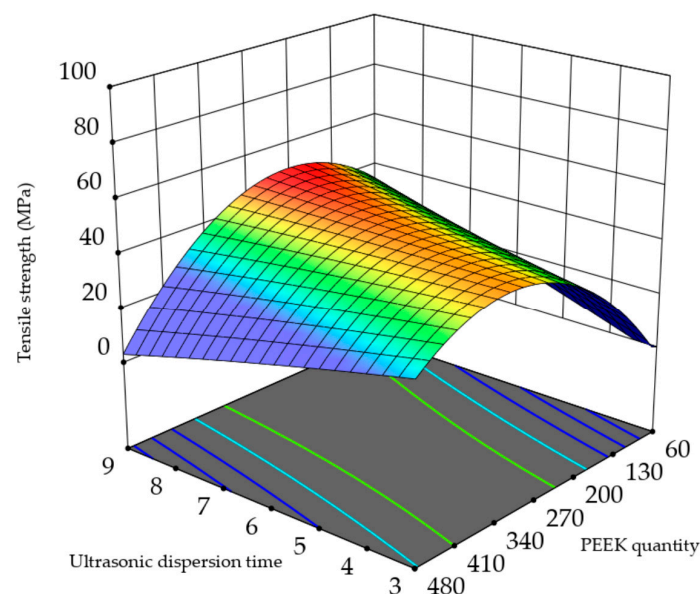


Figure 16. Effect of PEEK quantity and ultrasonic dispersion time on tensile strength when the pore size of the filter paper is 0.8 μm .

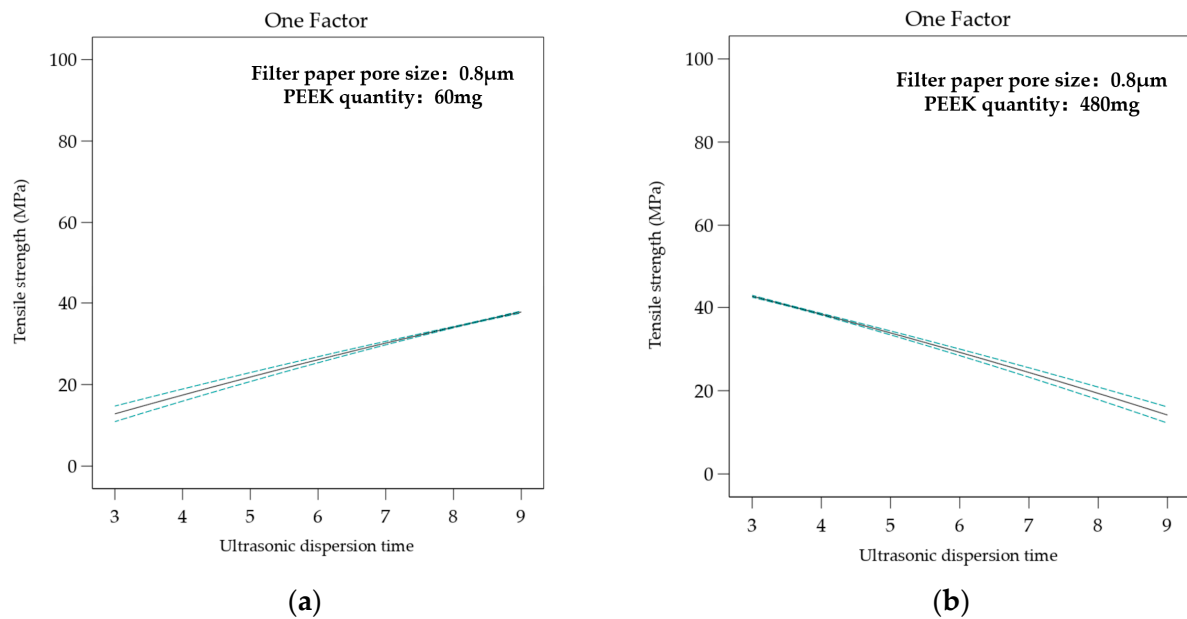


Figure 17. Effect of ultrasonic dispersion time on tensile strength when the pore size of the filter paper is 0.8 μm : (a) Effect of ultrasonic dispersion time when the PEEK quantity is 60 mg. (b) Effect of ultrasonic dispersion time when the PEEK quantity is 480 mg.

Figure 18 demonstrates that the interactive influence of PEEK content and filter paper pore size on tensile strength is minimal, corroborating the conclusions derived from the quadratic regression equation. With the enlargement of the filter paper pores, tensile strength exhibits a trend of an initial decrease followed by an increase. Conversely, as the PEEK content escalates, tensile strength manifests an initial increase followed by a decrease, with almost no variation in the trend of the curve. Figure 18 shows the PEEK quantity and ultrasonic dispersion time interaction effects

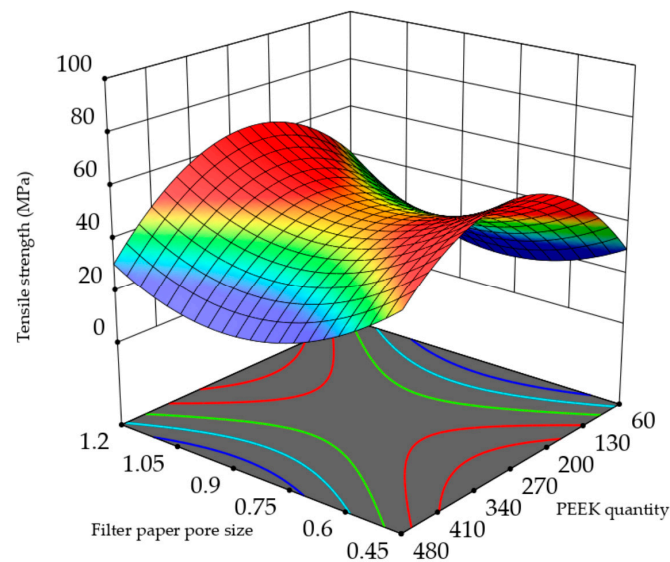


Figure 18. Effect of PEEK quantity and filter paper pore size on tensile strength when the ultrasonic dispersion time is 6 h.

4.3. Prediction of Optimal Process Parameters and Experimental Validation

The previous section analyzes the effects of various factors on the elasticity modulus and tensile strength from both single-factor and interaction perspectives. By utilizing the quadratic model and fitted equations, optimal process parameter combinations with better

comprehensive outcomes can be predicted. Response surface methodology simulation and fitting indicate that when the filter paper pore size is $0.45\ \mu\text{m}$, ultrasonic time is 8.3145 h, and PEEK content is 336.524 mg, higher values of the combined elasticity modulus and tensile strength can be achieved. Based on these optimal parameters, composite films are prepared, and their mechanical performance is tested, yielding the following results. Figure 19 shows the curves of the optimized elastic modulus and tensile strength.

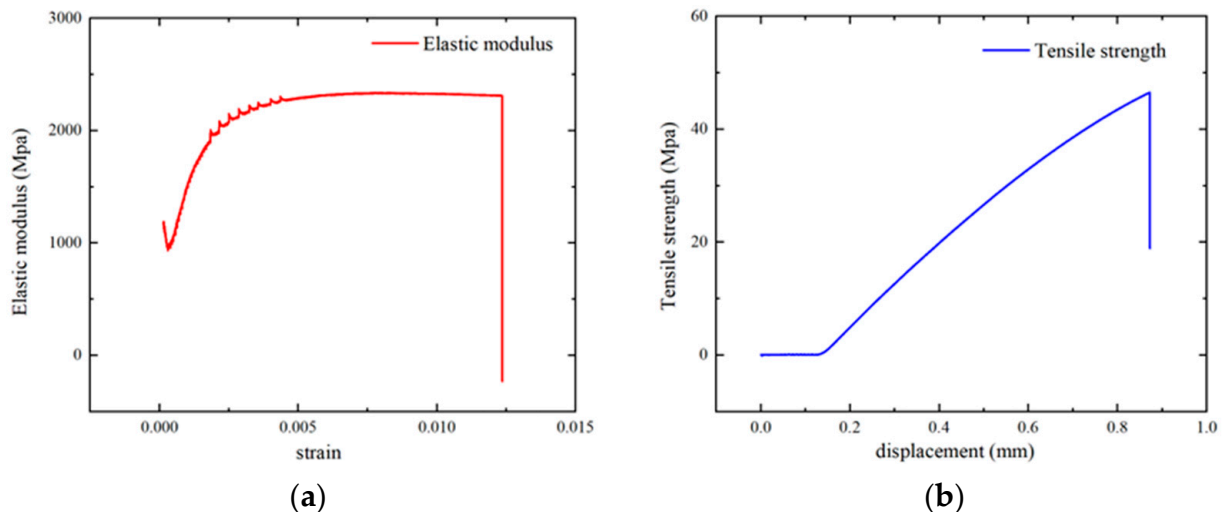


Figure 19. Optimum process parameters of film elastic modulus and tensile modulus: (a) Optimized elastic modulus change curve. (b) Optimized tensile strength variation curve.

The optimized elastic modulus and tensile strength are 2437.5723 MPa and 46.5196 MPa, respectively. It can be seen that the prediction model can predict the mechanical performance of the film very well, and the errors of the experimental and simulation results are 2.18% and 6.39%, respectively, which are in a reasonable range.

5. Conclusions

The mechanical performance of the films and the uniformity of the distribution of MWCNTs in the films are important factors affecting the enhancement effect. In this paper, MWCNTs/PEEK composite films are prepared by VSF. The paper is changed to improve the process of preparing the films and optimize the process parameters. The following conclusions can be drawn:

(1) Microscopic morphology observations indicate that when the MWCNT content is too high, they aggregate due to van der Waals forces, forming defects in the composite film. When the MWCNT content is too low, the PEEK matrix completely encapsulates the MWCNTs, rendering them ineffective for reinforcement. The ultrasonic dispersion time determines the uniform dispersion of MWCNTs/PEEK.

(2) The degree of influence of single factors on the mechanical performance of the film is as follows: PEEK content > ultrasonic time > filter paper pore size. The interaction effects on the mechanical performance of the film are as follows: filter paper pore size-ultrasonic time > ultrasonic time-PEEK content > filter paper pore size-PEEK content.

(3) With an increase in the filter paper pore size, the elasticity modulus initially increases and then decreases, while the tensile strength initially decreases and then increases. The influence of ultrasonic time on the elasticity modulus approximates a straight line; with more ultrasonic time, the elasticity modulus increases, and conversely, the tensile strength decreases. With an increase in PEEK content, the influence on the elasticity modulus initially decreases and then increases, while the tensile strength initially increases and then decreases.

(4) We predict a set of optimal parameters: filter paper pore size of 0.45 μm , ultrasonic time of 8.3 h, and PEEK content of 336.524 mg. Validation experiments conducted using these optimal process parameters yielded an elasticity modulus of 2437.5723 MPa and a tensile strength of 46.5196 MPa. The errors between the actual experimental results and the simulation results were 2.18% and 6.39%, respectively. These optimal process parameters increase the maximum value of the elasticity modulus by 12.3152% while maintaining a high tensile strength.

The study reveals that optimal process parameters facilitate MWCNTs to uniformly enhance the PEEK matrix. Such a homogeneous distribution permits load transfer and augments deformation and fracture resistance. Additionally, mechanical performance escalates via the inhibition of microcrack propagation and the facilitation of crack branching and bridging. Ultimately, the MWCNTs bolster the mechanical properties of the matrix, demonstrated by the elevated tensile strength and elastic modulus.

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