

Design and Preparation of Poly(aryl ether ketone)/Phosphotungstic Acid Hybrid Films with Low Dielectric Constant

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ABSTRACT: A material with low dielectric constant was produced using nanoparticle phosphotungstic acid (PWA) modified by the silane coupling agent γ -aminopropyltriethoxysilane (KH-550) dispersed in a poly(aryl ether ketone) containing (3-trifluoromethyl) phenyl side groups (FPEEK) matrix synthesized with (3-trifluoromethyl) phenyl hydroquinone (3FHQ) and 4,4'-difluorobenzophenone. The material was fabricated using solution-blending. Moreover, the dielectric, thermal, and mechanical properties of this material were characterized using a precision impedance analyzer, thermal gravimetric analyzer, and universal tester, respectively. The results indicate that modified PWA (*m*-PWA)/FPEEK composites show obvious improvement in the dielectric properties compared to unmodified PWA (*p*-PWA)/FPEEK composites. This should be attributed to the good dispersion and compatibility of *m*-PWA in FPEEK, as proven by scanning electron microscope and wide-angle X-ray diffraction. Besides, *m*-PWA/FPEEK composites also exhibited the relatively good thermal and mechanical properties. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3219–3225, 2013

KEYWORDS: dielectric properties; composites; compatibilization; films

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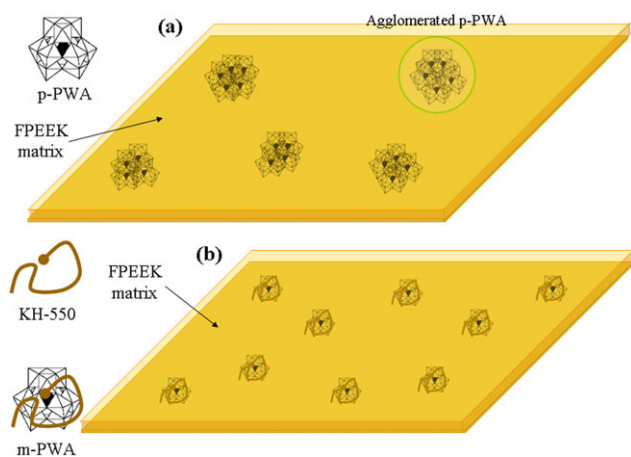
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INTRODUCTION

Poly(aryl ether ketone)s (PAEKs) are a class of important high-performance materials for microelectronic applications due to their excellent mechanical properties, good solvent resistance, size-accuracy, superior thermal stabilities as well as their low dielectric constant (κ) (3.2–3.5).^{1–5} With the development of microelectric industry, the next generation insulators are required to possess ultra-low κ with the value below 2.5 (1 MHz). In the past decade, a number of techniques have been explored for the preparation of low dielectric constant high performance materials, including (i) introduction of voids into polymer matrix by foaming processes^{6–8}; (ii) incorporation of fluorinated substituent into polymers^{9–13}; and (iii) embedment of nanoporous inorganic or organic particles into polymers.^{14–16} The low dielectric constant PAEKs obtained by first methods, sometimes, exhibit poor thermal and mechanical properties. The second method could lower the dielectric constant and improve the soluble of pure PAEKs, but only depending on incorporation of fluorinated substituent into PAEKs is difficult to reduce the dielectric constant at a ultra-low degree with the value below 2.5 (1 MHz). The third method has attracted great interest recently because the dielectric constant of polymers can be remarkably

decreased without severely affecting their thermal and mechanical properties. So in recent years, to obtain low dielectric constant materials with high performance, porous nanoparticles with stiff structures like polyhedral oligomeric silsesquioxanes (POSS) and polyoxometalates (POMs) have attracted more and more attention.^{17,18} However, POSS is usually very expensive and difficult to be obtained due to the complex purification processes and very low productivity. Comparing with POSS the POMs, which are a class of discrete, molecularly defined, nanosized inorganic metal oxide clusters, also have controlled porosity and more importantly, are easy to be synthesized. So employing the inorganic porous nanosized POMs into the polymer matrix to form low dielectric constant materials with high performance is an effective and economical method and has attracted more attention.^{19,20} However, before being introduced into the polymer matrix, the inorganic POM particles have to be modified with organic compounds or reactive unit to increase interactions with polymer matrix, otherwise, the POM clusters will take place very serious agglomeration in polymer matrix and may seriously affect the properties of the composites.

On the basis of the above analysis, PAEKs synthesized with (3-trifluoromethyl) phenyl hydroquinone (3FHQ) and 4,4'-



Scheme 1. Schematic diagram of (a) *p*-PWA/FPEEK hybrid films, (b) *m*-PWA/FPEEK hybrid films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

difluorobenzophenone (DFB) and Keggin-type nanoparticle phosphotungstic acid (PWA) that was a sort of the POM modified by the silane coupling agent γ -aminopropyltriethoxysilane (KH-550) were respectively chosen as the matrix and the filler in the preparation of a low- κ material with relatively good mechanical and thermal properties. The soluble FPEEK was adopted due to the low dielectric constant, whereas the modified PWA (*m*-PWA) was used to achieve the better dispersion in FPEEK and further more effectively decrease the dielectric constant of FPEEK as compared to the unmodified PWA (*p*-PWA) (Scheme 1). Moreover, the effects of adding *m*-PWA on the dielectric, thermal, and mechanical properties of FPEEK are discussed.

EXPERIMENTAL

Materials

Toluene was purchased from Beijing Chemical Reagent. Anhydrous potassium carbonate and dimethylacetamide (DMAC) were supplied by Sinopharm Chemical Reagent, China. Tetramethylene sulfone (TMS) was obtained from Jinzhou Oil Refinery and purified by distillation by pressure reduction before use. γ -Aminopropyltriethoxysilane (KH-550) and PWA ($H_3PW_{12}O_{40} \cdot xH_2O$) were provided by Nanjing Fine Chemical, China and Jilin Industry and Trade, China, respectively. 3FHQ was synthesized in our lab according to the method that we had published before.¹² DFB was obtained from Changzhou Huashan Chemical, China. Poly(ether ether ketone) (PEEK) was prepared in our laboratory according to the standard procedures. All other

common reagents were obtained from commercial sources and used without further purification.

Characterization

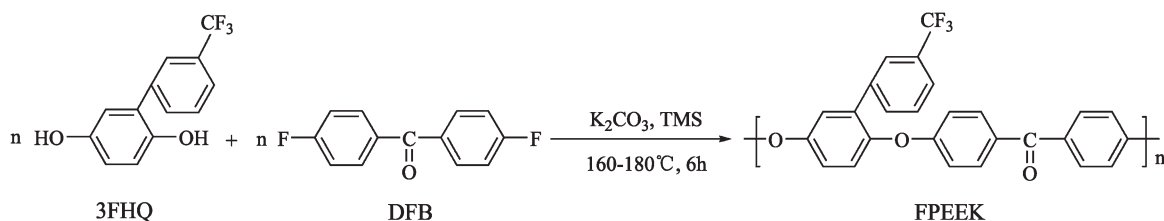
The FTIR spectrum (KBr) was measured using a Nicolet Impact 410 Fourier transform infrared spectrometer. Differential scanning calorimetry (DSC) measurements were performed on a Mettler-Toledo DSC 821^e instrument at a heating rate of $20^\circ C \text{ min}^{-1}$ under nitrogen. Thermal gravimetric analyses (TGA) were determined in a nitrogen atmosphere using a heating rate of $10^\circ C \text{ min}^{-1}$ and polymers were contained within open platinum pans on a Perkin-Elmer TGA-7. Mechanical properties of the thin films (about 0.1 mm, cast from DMAc solvents onto the glass plates, and followed by heating at $120^\circ C \text{ in vacuo}$) were evaluated at room temperature on a Shimadzu AG-I Universal Tester without strain gauge type extensometer at a strain rate of 10 mm min^{-1} . The dielectric constants of the polymer films (area $5.5 \times 5.5 \text{ mm}^2$ and thickness 0.1–0.2 mm, prepared by casting from DMAc solvents onto the glass plates and drying at $120^\circ C \text{ in vacuo}$, and then coated with silver by a vacuum evaporation method) were obtained using a Hewlett-Packard 4285A apparatus at room temperature and the frequency was 10^3 – 10^6 Hz . The crystallization behavior of the *m*-PWA clusters in the polymer matrix was investigated by Rigaku D/max-2500 X-ray diffractometer with $CuK\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) as the X-ray source. Energy dispersive spectrometer (EDS) and SEM images were obtained from a SSX-550, Shimadzu equipped with energy dispersive X-ray scanning electron microscope.

Synthesis of the Soluble FPEEK with Low Dielectric Constant

The soluble FPEEK with low dielectric constant as polymer matrix was synthesized via aromatic nucleophilic substituted reaction as depicted in Scheme 2. The synthesis procedure and the structure of the FPEEK polymer matrix had been published in our previous articles.^{12,21}

Preparation of *p*-PWA/FPEEK and *m*-PWA/FPEEK Hybrid Films

First, the Keggin-type PWA ($H_3PW_{12}O_{40} \cdot xH_2O$) was heated at $180^\circ C$ to remove its crystal water and got the PWA ($H_3PW_{12}O_{40}$). Then 0.05 g PWA was dissolved in 10 mL DMAc at room temperature to obtain the pure PWA (*p*-PWA) solution, at the same time, 1 g FPEEK was dissolved in 5 mL DMAc at room temperature to gain the FPEEK solution. Last, the FPEEK solution was directly mixed with the *p*-PWA solution, after stirring for 12 h, the mixed solution was cast on glass substrate, and the 5 wt % *p*-PWA/FPEEK hybrid film was obtained by heating to remove the DMAc solvent in vacuum oven. The synthesis procedure of 10 wt % *p*-PWA/FPEEK hybrid film was



Scheme 2. Synthesis of the soluble FPEEK with low dielectric constant.

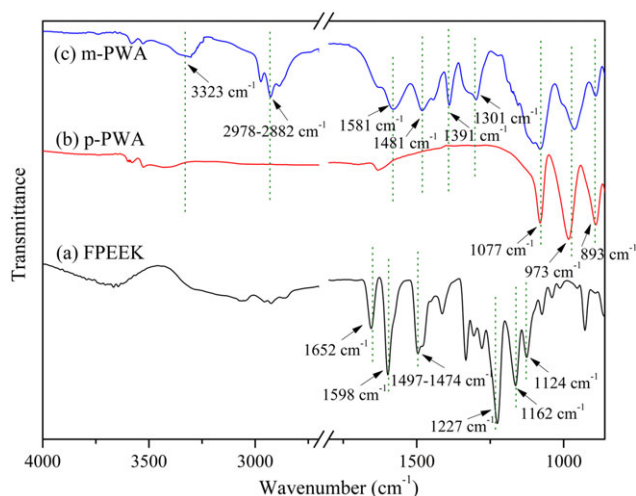


Figure 1. FTIR spectra of (a) pure FPEEK, (b) *p*-PWA, and (c) *m*-PWA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

as same as the method described above, only changed the addition amount of PWA to 0.1 g. Further, 0.05 g PWA was dissolved in 10 mL DMAc in the flask at room temperature, then the same mole amounts of KH-550 as that of the PWA and three times mole amounts of distilled water were added into the flask, the solution was stirred at room temperature for 24 h to get the modified PWA (*m*-PWA) solution, at the same time, 1 g FPEEK was dissolved in 5 mL DMAc at room temperature to gain the FPEEK solution. Last, the FPEEK solution was mixed with the above *m*-PWA solution, after stirring for 12 h, the mixed solution was cast on glass substrate and the 5 wt % *m*-PWA/FPEEK hybrid films were obtained by heating to remove the DMAc solvent in vacuum oven. The synthesis procedure of other weight percentage (wt %) *m*-PWA/FPEEK hybrid films were as same as the method described above, only changed the addition amount of PWA, KH-550 and distilled water.

RESULTS AND DISCUSSION

Chemical structures of FPEEK, *p*-PWA, and *m*-PWA

The chemical structures of FPEEK, *p*-PWA and *m*-PWA were confirmed by FTIR (KBr) spectra as shown in Figure 1(a–c), respectively. From Figure 1(a), the chemical structure of the FPEEK polymer matrix could be confirmed: 1124 and 1162 cm^{-1} ($-\text{CF}_3$ groups), 1227 cm^{-1} (Ar–O–Ar in the main chain), 1497–1474 cm^{-1} and 1598 cm^{-1} (benzene ring), 1652 cm^{-1} (C=O bond of aromatic ketone in the main chain). From the comparison of Figure 1(b,c), the chemical structures of the *p*-PWA and *m*-PWA were confirmed: 893 cm^{-1} (bridging oxygen W–O–W of PWA), 973 cm^{-1} (terminal oxygen W=O of PWA), 1077 cm^{-1} (P–O band of PWA), 1301, 1391, 1481, and 2978–2882 cm^{-1} (methylene of KH-550 of *m*-PWA), 1581 cm^{-1} (N–H of KH-550 of *m*-PWA), 3323 cm^{-1} (O–H of KH-550 of *m*-PWA).

Dielectric Properties of *m*-PWA/FPEEK and *p*-PWA/FPEEK Hybrid Films

Figure 2(a,b) presents the dielectric constant (κ) of *m*-PWA/FPEEK and *p*-PWA/FPEEK hybrid films at the frequency range from 1000 Hz to 1 MHz, respectively. Table I summarizes the dielectric constant and dielectric loss of *m*-PWA/FPEEK and *p*-PWA/FPEEK hybrid films at 1 MHz. One could find that the dielectric constants of these *m*-PWA/FPEEK hybrid films were ranged from 2.28 to 2.62 at 1 MHz and the κ -values were remarkable lower than that of the pure FPEEK film ($\kappa = 2.74$ at 1 MHz) under the same measurement conditions. Moreover, the dielectric constant of the *m*-PWA/FPEEK composites gradually decreased with the increasing *m*-PWA contents. A remarkable decrease of the dielectric constant for *m*-PWA/FPEEK composites (at 1 MHz) could be achieved, which the dielectric constant decreased from 2.74 for pure FPEEK polymer matrix to 2.28 for the composite with 10 wt % *m*-PWA. Presumably, for these *m*-PWA/FPEEK composites, the rigid and bulky PWA unit, which modified by silane coupling agent γ -aminopropyltriethoxysilane (KH-550) could keep nanosized dispersion in polymer matrix. As a result, the increased interface within the

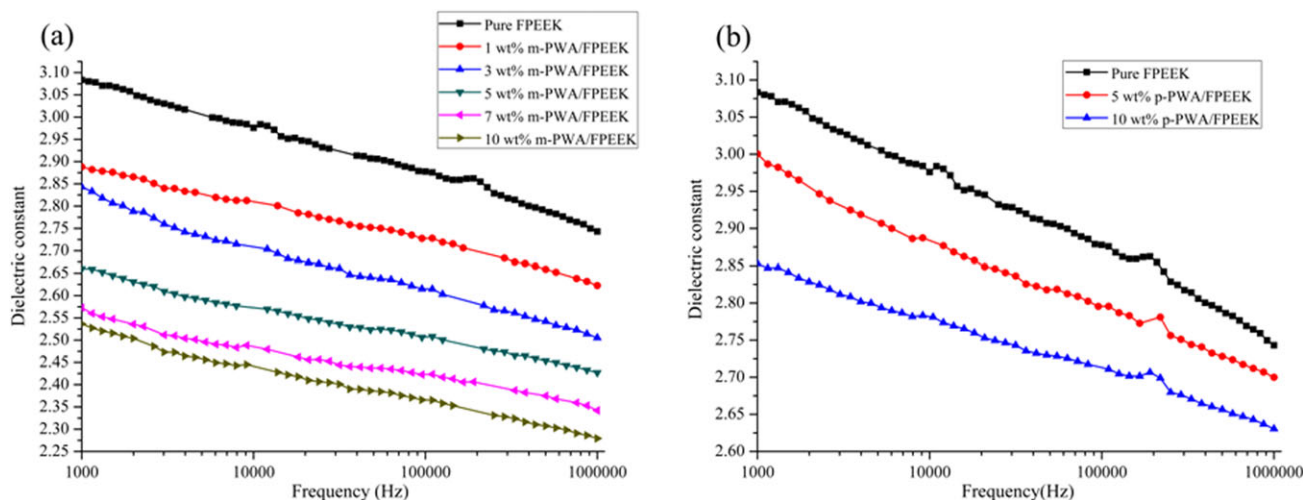


Figure 2. Frequency dependence of dielectric constant of (a) *m*-PWA/FPEEK hybrid films and (b) *p*-PWA/FPEEK hybrid films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Dielectric Properties of *m*-PWA/FPEEK and *p*-PWA/FPEEK Hybrid Films

Sample	Dielectric constant (κ) (at 1 MHz)	Dielectric constant decrease ($\Delta\kappa$)	Dielectric loss (at 1 MHz)
Pure FPEEK	2.74	-	0.01611
1 wt % <i>m</i> -PWA/FPEEK	2.62	-0.12	0.00608
3 wt % <i>m</i> -PWA/FPEEK	2.50	-0.24	0.00606
5 wt % <i>m</i> -PWA/FPEEK	2.42	-0.32	0.00425
7 wt % <i>m</i> -PWA/FPEEK	2.34	-0.40	0.00326
10 wt % <i>m</i> -PWA/FPEEK	2.28	-0.46	0.00232
5 wt % <i>p</i> -PWA/FPEEK	2.70	-0.04	0.00522
10 wt % <i>p</i> -PWA/FPEEK	2.63	-0.11	0.00403

polymer matrix and nanosized *m*-PWA clusters in the composites might lead to a strong self-polarization-induced radical localization of electronic density at the hetero-junction. The strong self-polarization-induced and the intrinsic pores of PWA particles could remarkably decrease the κ -values of FPEEK composites.^{22–24} In contrast, one could find that the *p*-PWA/FPEEK hybrid films had the κ -value of 2.70 and 2.63 at 1 MHz when the PWA content was 5 and 10 wt %, respectively. The dielectric constants of the *p*-PWA/FPEEK hybrid films were only slightly lower than that of pure FPEEK matrix ($\kappa = 2.74$ at 1 MHz)

under the same measurement conditions. This result might be due to the agglomerated *p*-PWA unit in the *p*-PWA/FPEEK hybrid films tended to exclude the close contact with surrounding polymer matrix chains and free volume around the agglomerated PWA unit was created. The free volumes and the intrinsic pores of PWA particles resulted in the decreased κ -value. But the agglomerated PWA unit lost the unique self-polarization-induced effect of nanoparticles, so the dielectric constant of the hybrid films was only decreased in a limited extent. In summary, the self-polarization-induced effect of nanoparticles was mainly responsible for the remarkable decrease of dielectric constant for the composites. Therefore, it was very important that the PWA particles modified by the suitable method in nanometer size were dispersed in polymer matrix. Table I shows that the dielectric loss factors of these hybrid films at 1 MHz are very low and the dielectric loss factors of the *m*-PWA/FPEEK hybrid films are lower than that of the *p*-PWA/FPEEK hybrid films. Thus, this modified method was an effective and simple way to decrease the dielectric constant of the polymer matrix.

The Morphologies of *m*-PWA/FPEEK and *p*-PWA/FPEEK Hybrid Films

Figure 3 shows SEM photographs of the fracture surfaces of the *m*-PWA/FPEEK and *p*-PWA/FPEEK hybrid films. For the *m*-PWA/FPEEK films [Figure 3(a,b)], it could be seen that the surface protuberances resulting from the modified PWA clusters were homogeneously distributed in the whole film and the size of the visible particles was about 30 nm. Moreover, the number

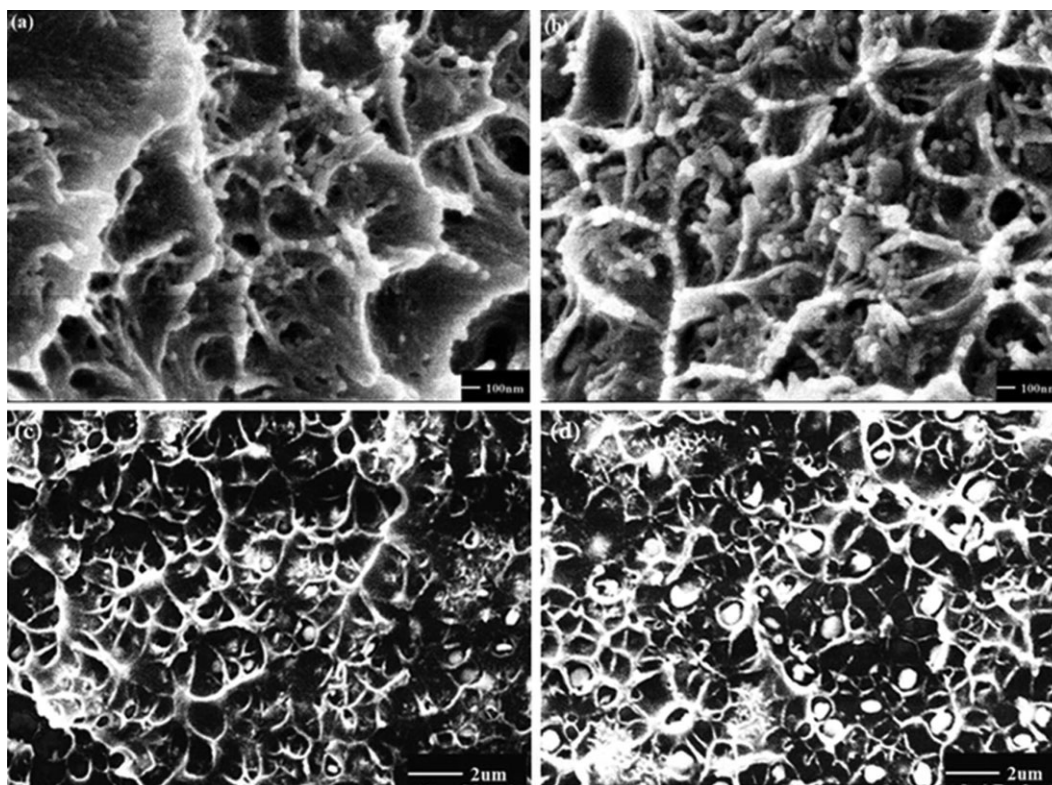


Figure 3. Scanning electron microscope photographs of (a) 5 wt % *m*-PWA/FPEEK hybrid film, (b) 10 wt % *m*-PWA/FPEEK hybrid film, (c) 5 wt % *p*-PWA/FPEEK hybrid film, and (d) 10 wt % *p*-PWA/FPEEK hybrid film.

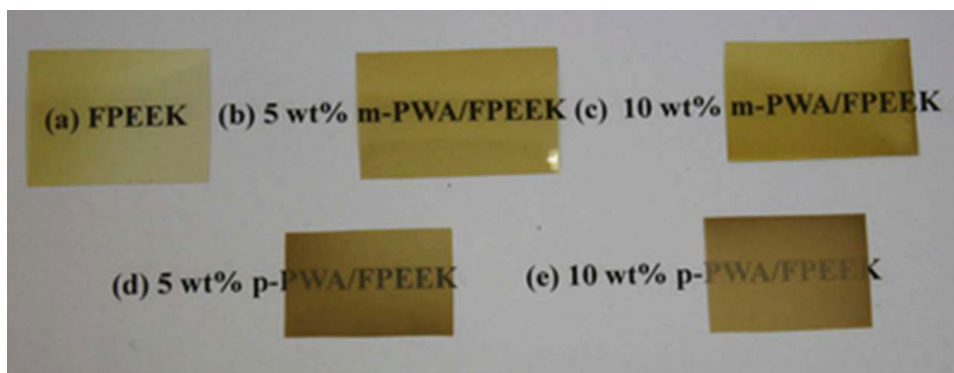


Figure 4. Images of (a) pure FPEEK film, (b) 5 wt % *m*-PWA/FPEEK hybrid film, (c) 10 wt % *m*-PWA/FPEEK hybrid film, (d) 5 wt % *p*-PWA/FPEEK hybrid film, and (e) 10 wt % *p*-PWA/FPEEK hybrid film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of protuberances increased with the increase of PWA content, to some extent reflecting the increase of free volume in these hybrid films. In contrast, that unmodified PWA particles was directly mixed with the FPEEK polymer matrix would result in very serious agglomeration as shown in Figure 3(c,d), and the size of the agglomerated PWA particles was about 1 μm as well as the agglomerated PWA particles was easy to lose. Besides, from the digital photographs in Figure 4, it could be demonstrated that the *p*-PWA/FPEEK hybrid films showed the poor transparency. This result clearly suggested that the addition of silane coupling agent γ -aminopropyltriethoxysilane (KH-550) could improve the dispersion of the PWA particles in the FPEEK matrix. It also confirmed the speculation that the dielectric constants of the *m*-PWA/FPEEK hybrid films were lower than that of the *p*-PWA/FPEEK hybrid film due to the good dispersion in above section.

The Crystallization Behavior of *m*-PWA/FPEEK Hybrid Films

In Figure 5, the solid state pure PWA exhibited multiple sharp diffraction peaks at $2\theta = 8.9^\circ; 10.5^\circ; 12.8^\circ; 14.9^\circ; 18.2^\circ; 21.0^\circ; 23.5^\circ; 25.8^\circ; 27.9^\circ; 29.8^\circ; 31.7^\circ; 33.5^\circ; 35.2^\circ$, and 38.3° , respec-

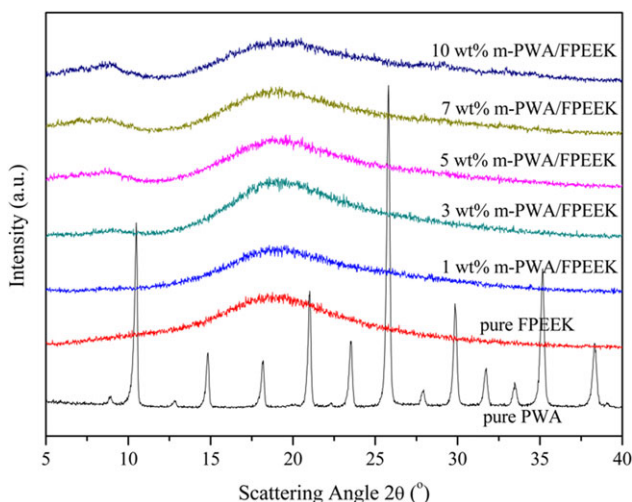


Figure 5. WAXD profiles of pure PWA, FPEEK, and *m*-PWA/FPEEK hybrids films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tively, suggesting that the pure PWA formed apparently crystalline structure. The pure FPEEK only exhibited a diffuse peak at $2\theta = 18.8^\circ$, whereas the *m*-PWA/FPEEK composites exhibited two diffuse peaks at $2\theta = 18.8^\circ$ and $2\theta = 8.8^\circ$, respectively. The diffuse peak indicated that the modified PWA clusters could not form perfect crystal domains in the FPEEK matrix and the FPEEK polymer matrix and these composites exhibited amorphous structures, because the crystalline polymers would display sharp diffraction peaks. This result suggested that the *m*-PWA nanoparticles were successfully incorporated into the polymer matrix and retained their nanoscaled dimensions in the polymer matrix.²⁵ Moreover, the addition of silane coupling agent γ -aminopropyltriethoxysilane (KH-550) could enhance the compatibility between PWA and FPEEK in the composites and further improve the dispersion of PWA in the FPEEK matrix. Also, the crystallization behavior of *m*-PWA/PEEK hybrid films was characterized by the following DSC characterization results.

The Dispersion of Modified PWA in *m*-PWA/FPEEK Hybrid Films

EDS is an effective method to observe the distribution of inorganic elements in a polymer matrix as it provides clear and direct information regarding the distribution and quantity of each element in the sample. A single PWA ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) particle contains 12 tungsten atoms. Thus, W-mapping of EDS is an easy and convenient method to observe the distribution of modified PWA clusters in the *m*-PWA/FPEEK hybrid films. The W-mappings of *m*-PWA/FPEEK composites with varied amounts of *m*-PWA were shown in Figure 6. Each sample was observed at magnifications of 40 k. The well-dispersed red dots representing the position of the tungsten element illustrated that *m*-PWA particles were well dispersed in FPEEK matrix and the number of the red dots increased with the increase of *m*-PWA content. This result further suggested that the modification of PWA by silane coupling agent γ -aminopropyltriethoxysilane (KH-550) could increase the dispersion of the PWA nanoparticles in the FPEEK matrix.

Thermal Properties of *m*-PWA/FPEEK Hybrid Films

The glass transition temperature (T_g) and TGA data of pure FPEEK and *m*-PWA/FPEEK composites are listed in Table II. It is clear that the T_g values of *m*-PWA/FPEEK composites gradually decrease with the increasing of *m*-PWA content. The T_g

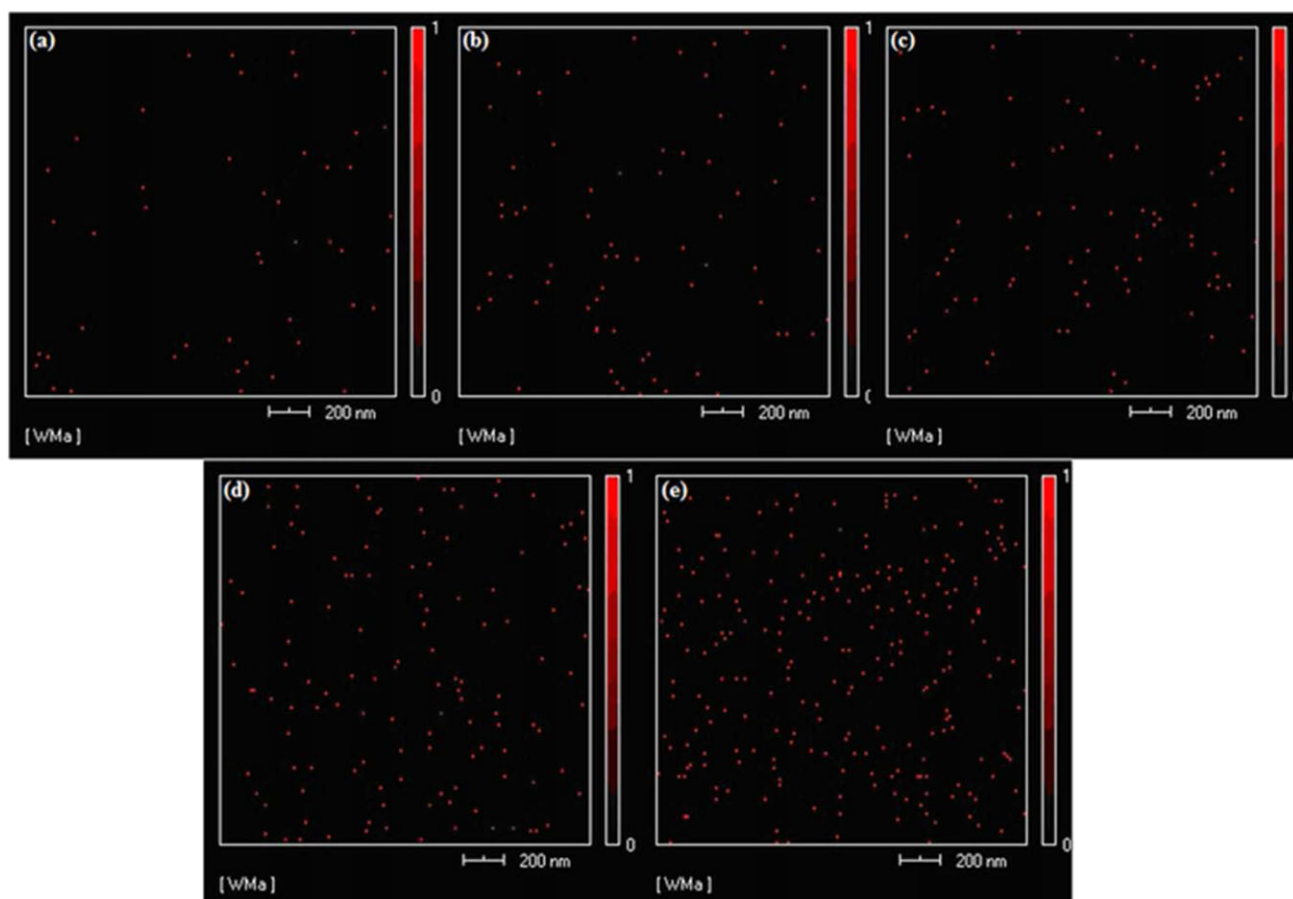


Figure 6. W-mapping of *m*-PWA/FPEEK hybrid films (a) 1 wt % *m*-PWA/FPEEK, (b) 3 wt % *m*-PWA/FPEEK, (c) 5 wt % *m*-PWA/FPEEK, (d) 7 wt % *m*-PWA/FPEEK, and (e) 10 wt % *m*-PWA/FPEEK hybrids films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

value of pure FPEEK was 136°C, whereas the T_g value of the composite with 10 wt % of *m*-PWA clusters decreased 12°C. Just as the indication of the dielectric constant values, which have been discussed above, the free volume of the composites

Table II. Thermal Properties of *m*-PWA/FPEEK and *p*-PWA/FPEEK Hybrid Films

Sample	T_g (°C) ^a	DT ₅ (°C) ^b	DT ₁₀ (°C) ^c
Pure FPEEK	136	496	514
1 wt % <i>m</i> -PWA/FPEEK	130	484	503
3 wt % <i>m</i> -PWA/FPEEK	129	471	484
5 wt % <i>m</i> -PWA/FPEEK	128	457	473
7 wt % <i>m</i> -PWA/FPEEK	127	444	463
10 wt % <i>m</i> -PWA/FPEEK	124	428	444
5 wt % <i>p</i> -PWA/FPEEK	130	491	509
10 wt % <i>p</i> -PWA/FPEEK	126	489	505

^aFrom the second heating trace of DSC measurements conducted at a heating rate of 20°C min⁻¹.

^bFive percent weight loss temperatures measured by TGA at a heating rate of 10°C min⁻¹ in N₂.

^cTen percent weight loss temperatures measured by TGA at a heating rate of 10°C min⁻¹ in N₂.

increased with the increasing of the PWA contents. Thus the greater free volume generally resulted in a lower value of T_g for polymer matrix. As shown in Table II, the TGA data DT₅ and DT₁₀ of *m*-PWA/FPEEK composites were gradually decreased upon incorporation of *m*-PWA contents. Comparing with pure FPEEK, the lower decomposition temperature of *m*-PWA/FPEEK composites might originate from the thermal degradation of silane coupling agent KH-550. It was noteworthy that the incorporation of 10 wt % *m*-PWA only decreased the DT₅ of the composite to 428°C from 496°C (Pure FPEEK) and decreased the DT₁₀ of the composite to 444°C from 514°C (Pure FPEEK). The results indicated that the *m*-PWA/FPEEK composites also exhibited excellent thermal properties.

Mechanical Properties of *m*-PWA/FPEEK Hybrid Films

The mechanical properties of the hybrid films are summarized in Table III. The hybrid films had tensile strength of 31.0–95.5 MPa, Young's modulus of 1.48–2.69 GPa, and elongation at break of 1.4–31.7%. Their tensile strength and elongation at break decreased with the increase of inorganic nanoparticle PWA, while the Young's modulus increased. Overall, *m*-PWA/FPEEK hybrid films still exhibited enough high strength and modulus.

Table III. Mechanical Properties of *m*-PWA/FPEEK Hybrid Films

Sample	Tensile strength (MPa)	Tensile strength decrease (%)	Young's modulus (GPa)	Young's modulus increase (%)	Elongation at break (%)	Elongation at break decrease (%)
FPEEK	95.5	-	1.48	-	31.7	-
1 wt % <i>m</i> -PWA/FPEEK	61.6	35.5	2.47	66.9	3.3	89.6
3 wt % <i>m</i> -PWA/FPEEK	61.9	35.2	2.69	81.8	3.1	90.2
5 wt % <i>m</i> -PWA/FPEEK	67.5	29.3	2.50	68.9	2.0	93.7
7 wt % <i>m</i> -PWA/FPEEK	39.2	58.9	2.22	50.0	1.5	95.3
10 wt % <i>m</i> -PWA/FPEEK	31.0	67.5	2.44	64.9	1.4	95.6

CONCLUSIONS

The modified and unmodified mono-lacunary Keggin-type PWA nanoparticles (*m*-PWA and *p*-PWA) were introduced into the soluble low dielectric constant FPEEK matrix by solution blending method and the low- κ *m*-PWA/FPEEK and *p*-PWA/FPEEK composites were fabricated. The better nanoscale dispersion of the *m*-PWA particles in FPEEK matrix resulted from the modification of PWA using silane coupling agent γ -aminopropyltriethoxysilane (KH-550) as compared to *p*-PWA. As a result, the dielectric constants of *m*-PWA/FPEEK composites more remarkably decreased. A low κ of 2.28 was achieved at the frequency of 1 MHz when *m*-PWA content reached 10 wt % in the *m*-PWA/FPEEK composites. In contrast, the κ value of the *p*-PWA/FPEEK composite merely decreased to 2.63 from 2.74 of FPEEK matrix at 1 MHz when the *p*-PWA had the same content of 10 wt %. The remarkable decreased dielectric constant of the *m*-PWA/FPEEK composites should be due to the combination of self-polarization-induce effect of the PWA nanoparticles and the intrinsic porosity of the PWA particles. Especially the self-polarization-induce effect, the agglomerated PWA in *p*-PWA/FPEEK lost the unique self-polarization-induce effect of nanoparticles, so the dielectric constant of the *p*-PWA/FPEEK hybrid films only decreased in a limited extent. The thermal and mechanical properties of the *m*-PWA/FPEEK composites with good dielectric properties were slightly decreased with the content increase of inorganic *m*-PWA particles, but the *m*-PWA/FPEEK composites still exhibited favorable thermal and mechanical properties.

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