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Micro/Mesoporous Fe₃O₄/Fe-Phthalocyanine Microspheres and Effects of Their Surface Morphology on the Crystallization and Properties of Poly(Arylene Ether Nitrile) Composites

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Abstract: The surface morphology of nanoparticles significantly affects the final properties and interfacial characteristics of their composites. Thus, investigations on the surface morphology of the nanoparticles is essential to fabricate improved nanoparticle-reinforced composites. Fe₃O₄/Fe-phthalocyanine (FePc) hybrid microspheres with micro/mesoporous structures were prepared via a solvothermal process and solvent etching method. The surface morphology and compositional distribution were respectively investigated using a scanning electron microscope (SEM) and a transmission electron microscope (TEM) to rule out that FePc monomers have been blended with Fe_3O_4 to form Fe_3O_4 /FePc hybrid microspheres without serious agglomeration. The surface roughness of Fe₃O₄/FePc microspheres was investigated by the scanning probe microscope (SPM), and confirmed by the adsorption and desorption isotherms of N₂. The effects of the various surface morphologies on the crystallization behavior of crystallizable poly(arylene ether nitrile) (c-PEN) were first employed to confirm the surface characteristics of the resulted microspheres. Results indicated that the etched $Fe_3O_4/FePc$ microspheres would improve the crystallization degree of *c*-PEN, due to their much more micro/mesoporous structures than that of original Fe₃O₄/FePc. Then, Fe₃O₄/FePc hybrid microspheres reinforced PEN composite films were prepared and their interfacial compatibility was monitored using an SEM. Excellent thermal stability and improved mechanical properties were obtained by combining the etched Fe₃O₄/FePc and PEN matrix. The excellent surface properties and micro/mesoporous structures make the novel Fe₃O₄/FePc an excellent candidate of organic/inorganic hybrid fillers and micro/mesoporous materials.

Keywords: micro/mesoporous; Fe₃O₄/FePc hybrid microspheres; adsorption and desorption; interfacial properties; poly(arylene ether nitrile) composite

1. Introduction

In the field of polymeric matrix composites, the interface compatibility between reinforcement and polymeric matrices is one of the most important factors that influence the composite properties [1–3]. When the reinforcement was an inorganic filler, especially ceramic, the interface compatibility between the reinforcement and polymeric matrix was poor [4]. Therefore, the technology of the filler modified branch has been extensively studied [5,6]. Organic/inorganic hybrids are an important method to improve the surface properties of an inorganic filler, because the organic component can increase the interface interaction between fillers and polymeric matrices [7]. Fe₃O₄/FePc hybrid microspheres are unique magnetic nano-fillers, and the existence of Fe-phthalocyanine (FePc) not only offered the polar



microspheres makes the microsphere and polymer matrix lack compatibility at the nanometer scale. Nowadays, humans pay more attention to micro/mesoporous structure materials for their high surface area and excellent surface properties [9,10]. The applications of micro/mesoporous structure materials are extensive in adsorption and separation, catalyst carrier, membrane separation, and energy storage applications [11–15]. To date, a lot of preparation methods of micro/mesoporous structure materials have been obtained including templating [16], recrystallization [17], and dealumination/desilication [18], etc. However, most of these preparation methods were post-processing with a high temperature to obtain a large number of micro/mesoporous. Moreover, the treatment may significantly destroy the organic components. Compared with these methods, solution etching is a more simple and easy way to prepare porous materials. The degree of etching can be controlled easily by tuning the etching conditions. Thus, organic/inorganic hybrid micro/mesoporous materials can be obtained with etching methods.

In this work, a novel kind of micro/mesoporous $Fe_3O_4/FePc$ hybrid microspheres was designed and prepared via an etching method. The micromorphology of the etched $Fe_3O_4/FePc$ hybrid microspheres were investigated in detail with SEM, TEM, SPM, and the adsorption and desorption isotherms of N₂. To further study the effects of the micro/mesoporous morphology on the interfacial properties of their composites, a kind of crystallizable poly(arylene ether nitrile) (*c*-PEN) were selected to confirm the morphology of the $Fe_3O_4/FePc$ hybrid microspheres on the crystallization. Then, the high-performance PEN was also selected to study the dielectric, mechanical, and thermal properties of $Fe_3O_4/FePc/PEN$ hybrid microsphere composites.

2. Materials and Methods

2.1. Materials

N-methylpyrrolidone (NMP, 99%) was purchased from Tianjin BODI chemicals, Tianjin, China. Tetrahydrofuran (THF, 99%), FeCl₃·6H₂O (99%), NaAc·3H₂O (99%), and ethylene glycol (EG) (99.5%) were purchased from Kelong Reagent Co. Ltd., Chengdu, China. Tri-substituted-bisphthalonitrile (TPH) was prepared in our laboratory [19]. Polyethylene glycol (PEG 2000) was purchased from Tianjin Zhiyuan Reagent Co. Ltd., Tianjin, China. Two kinds of different molecular weight polyarylene ether nitriles (PEN) were synthesized in our laboratory [20,21].

2.2. Preparation of Original Fe₃O₄/FePc Magnetic Hybrid Microspheres

In our previous work, the synthetic procedure of $Fe_3O_4/FePc$ hybrid microspheres was reported [22,23]. In this work, the synthetic route of the $Fe_3O_4/FePc$ was according to following procedure with a little modification: $FeCl_3 \cdot 6H_2O$ (11.8 g) was dissolved in EG (200 mL) at room temperature, followed by the addition of PEG 2000 (8.15 g) and TPH (3.5 g) to form an orange solution with the help of an ultrasonic bath. The NaAc $\cdot 3H_2O$ (31.5 g) was slowly added into the solution with vigorous stirring for 30 min and then poured in a Teflon-lined stainless-steel autoclave. The autoclave was heated and maintained at 200 °C for 15 h, then allowed to cool to room temperature. The products were filtered and washed several times with ethanol and distilled water, then dried at 60 °C for 10 h. The original $Fe_3O_4/FePc$ hybrid microsphere was obtained and labeled as $O-Fe_3O_4/FePc$.

2.3. Preparation of Etched Fe₃O₄/FePc Hybrid Microspheres

The Fe₃O₄/FePc hybrid microspheres were added into the NMP solvent treated by ultrasonic wave at room temperature and stirring for 1 h. Then, the mixture was treated at 80 °C for 24 h with vigorous stirring. After being separated, the sample was washed several times with ethanol and distilled water and dried at 60 °C for 12 h. The obtained microspheres were named as etched Fe₃O₄/FePc hybrid microspheres (*E*-Fe₃O₄/FePc).

2.4. Preparation of Crystallizable PEN Coated Fe₃O₄/FePc Magnetic Microspheres

The crystallizable PEN (*c*-PEN) was used to obtain the coated Fe₃O₄/FePc microspheres [4]. First, Fe₃O₄/FePc hybrid microspheres (0.6 g) were added into a 100 mL three-necked round-bottom flask loaded with 18 mL THF solvent and treated using ultrasonic waves for 2 h. Meanwhile, 0.3 g of *c*-PEN was dissolved in THF with stirring. After the *c*-PEN was dissolved completely, the Fe₃O₄/FePc hybrid microspheres suspension was added into the *c*-PEN solution with ultrasonic waves and stirring at 70 °C for 1 h. The mixture was placed in a rotary evaporator treated with ultrasonic waves until the THF was evaporated completely at 50 °C. Finally, the sample was ground into powder in a mortar, and heated at 280 °C for 4 h. With the steps above, the *c*-PEN coated *O*-Fe₃O₄/FePc and *E*-Fe₃O₄/FePc and *c*-PEN@*E*-Fe₃O₄/FePc, respectively. The obtained hybrid microspheres were treated at 280 °C for 4 h for the testing of X-ray powder diffraction (XRD) and Differential scanning calorimeter (DSC). For comparison, the neat *c*-PEN was also treated under the same conditions.

2.5. Preparation of Fe₃O₄/FePc Reinforced PEN Magnetic Nanocomposites

The high-performance weight PEN (*H*-PEN) and Fe₃O₄/FePc hybrid microspheres were blended and the composites were obtained via a solution casting method after continuous ultrasonic dispersion. The detailed processes were as follows: a certain amount of Fe₃O₄/FePc hybrid microspheres were added into a certain amount of NMP and treated using ultrasonic waves for 2 h. Then, the suspension solution was slowly added into the *H*-PEN solution with vigorous stirring and with an ultrasonic wave treatment at 80 °C for 0.5 h. Subsequently, the mixture was casted on a clear glass plate and dried in an oven with a procedure of 80 °C for 1 h, 80–200 °C for 6 h, and 200 °C for 2 h and 220 °C for 1 h to remove the solvent. According to the processes, various Fe₃O₄/FePc reinforced *H*-PEN magnetic nanocomposite films were obtained. For simplicity, the obtained films were named as neat *H*-PEN, *O*-Fe₃O₄/FePc/*H*-PEN, and *E*-Fe₃O₄/FePc/*H*-PEN, respectively.

2.6. Characterizations

The micromorphologies of the Fe₃O₄/FePc hybrid microspheres and PEN hybrid microsphere composite films were performed using a scanning electron microscope (SEM, JSM 5900 LV, Tokyo, Japan) and a transmission electron microscope (TEM, Hitachi H600, Tokyo, Japan). The detailed surface morphologies of O-Fe₃O₄/FePc and E-Fe₃O₄/FePc were performed using a scanning probe microscope (SPM, OLS4500, Olympus, Tokyo, Japan). The Brunauer-Emmett-Teller (BET) surface area and pore size distribution of O-Fe₃O₄/FePc and E-Fe₃O₄/FePc were explored by measuring N₂ adsorption-desorption at 77 K on an Autosorb-1 MP Autoumated Physisorption Analyzer.

The crystallization of the hybrid microsphere and the *H*-PEN hybrid microsphere composites were performed using X-ray powder diffraction (XRD, Rigaku (Tokyo, Japan) RINT2400 with Cu K α radiation). The thermally induced phase transition behaviors of the microspheres and *c*-PEN composites were performed on a TA Instrument DSC-Q100 (TA Instrument, New Castle, DE, USA) with a heating rate of 10 °C/min and a nitrogen flow rate of 50 mL/min from 40 °C to 360 °C. Thermal gravimetric analysis (TGA) of the *H*-PEN-based microspheres composites was carried out using a TA Instrument TGA-Q50 (TA Instrument, New Castle, DE, USA) with a heating rate of 20 °C/min from room temperature to 800 °C under a nitrogen atmosphere.

Dielectric property measurements of the *H*-PEN magnetic nanocomposites were carried out using a TH 2819A (Tonghui, Changzhou, China) precision LCR (Inductance, Capacitance, Resistance) meter. Furthermore, the electric breakdown strength of *H*-PEN hybrid microsphere composites was carried out using a Dielectric Withstand Voltage Tester (Air Times, Beijing, China). The mechanical property measurements of PEN microsphere composite films were investigated using a SANS CMT6104 Series Desktop Electromechanical Universal Testing Machine (SANS, Shengzhen, China).

3. Results

3.1. The Microcosmic Morphology of the Various Fe₃O₄/FePc

The various $Fe_3O_4/FePc$ microspheres were prepared using a solvothermal method, and then the microspheres were etched using NMP; the schematic illustration is shown in Scheme 1. Figure 1 shows the SEM images of O-Fe₃O₄/FePc and E-Fe₃O₄/FePc hybrid microspheres. It is obvious that the overall shape of the Fe₃O₄/FePc hybrid microspheres did not change too much after etching. However, the weight loss of the E-Fe₃O₄/FePc in comparison with that of O-Fe₃O₄/FePc was evaluated (\approx 15.4%). According to the designed Fe₃O₄/FePc, the weight of FePc was 51%; thus, the etched FePc was a fraction of the whole FePc in the Fe₃O₄/FePc microspheres. In the previous reports, the FePc was proved to be bonded with the Fe₃O₄ [24]. As mentioned above, it can be concluded that surplus FePc exists in the form of physical aggregation in the Fe₃O₄/FePc microspheres.



Scheme 1. The schematic illustration of the preparation of (**a**) the original $Fe_3O_4/FePc$ hybrid microspheres and (**b**) the etched $Fe_3O_4/FePc$ hybrid microspheres.



Figure 1. The SEM images of (a) O-Fe₃O₄/FePc and (b) E-Fe₃O₄/FePc.

Compared with that of *O*-Fe₃O₄/FePc, *E*-Fe₃O₄/FePc shows a little smaller diameter (\approx 150 nm), and the thickness of the micro/mesoporous regions on the edge of microsphere increases. It indicates that the FePc embedded into the Fe₃O₄/FePc was etched and the frame structure of Fe₃O₄ remained. Meanwhile, the center of *E*-Fe₃O₄/FePc appeared as a pale dot (Figure 2b,d). Furthermore, from the regions marked by the red square and arrow, we can find that the surface structure of the microspheres before and after etching was obviously different. This was because hot NMP can dissolve the organic fraction of the hybrid microsphere, and so the surface of the microsphere was easily accessible by the NMP. So, after the etching, the number of micro/mesoporous regions on the surface of Fe₃O₄/FePc microspheres increased significantly. Due to the fact that the NMP solvent had difficulty diffusing into the center region of the microspheres, only a small amount FePc was etched and scattered mesoporous regions were observed in *E*-Fe₃O₄/FePc. Moreover, the fact that the microsphere morphology was observed also indicates that the organic FePc was dispersed in the hybrid microspheres, and after being treated with NMP, the fracture structures of the Fe₃O₄/FePc was still remaining.



Figure 2. TEM images of (a,c) O-Fe₃O₄/FePc and (b,d) E-Fe₃O₄/FePc.

Figure S1 shows the change in color of the NMP solution before and after etching, and from the photo we can see that the color of NMP solution turned into a dark transparent solution. It indicated that the organic components were dissolved in the NMP solution after 24 h of heat etching. Figure S2 shows the UV-vis spectra of the etched NMP solution after filtering. One strong sharp peak and a small peak were recorded at 350 nm and 670 nm, respectively. The former one is attributed to the TPH, the latter one is ascribed to FePc. Meanwhile, the thermogravimetric analysis of the samples before and after etching were measured and are shown in Figure S3. It is obvious that the initial decomposition temperature of *O*-Fe₃O₄/FePc was lower than *E*-Fe₃O₄/FePc. This was because the organic components of the microsphere surface are more susceptible to the thermal decomposition. What is more, the ultimate char yield at 600 °C of the *E*-Fe₃O₄/FePc (85.7%) is higher than *O*-Fe₃O₄/FePc (81.2%). This indicates that the organic components of surface of the hybrid microsphere had been etched after 24 h heat etching.

Further, the surface microstructure of the hybrid microspheres was studied using SPM, as presented in Figure 3. From the 3-D images (Figure 3a,b), it is obvious that the dispersion of E-Fe₃O₄/FePc microspheres was better than that of the *O*-Fe₃O₄/FePc. In sight of the height of each microsphere, they were all between 100 nm and 150 nm. After being etched, the size of the E-Fe₃O₄/FePc microspheres became slightly smaller than that of the *O*-Fe₃O₄/FePc. As is well known, the Fe₃O₄/FePc microspheres are composed with the inorganic Fe₃O₄ and organic FePc. The hot NMP solvent will significantly dissolve the organic FePc on the surface of the microspheres, which will decrease the size of the Fe₃O₄/FePc microspheres. The 2-D SPM images of different microspheres are shown in Figure 3c,d. It indicates that the microspheres had rough surfaces and the roughness of the *E*-Fe₃O₄/FePc was obviously greater than that of *O*-Fe₃O₄/FePc.



Figure 3. SPM 5 μ m × 5 μ m images of *O*-Fe₃O₄/FePc ((**a**) 3D and (**c**) 2D) and *E*-Fe₃O₄/FePc ((**b**) 3-D and (**d**) 2-D).

3.2. The Surface Characteristics of the Various Fe₃O₄/FePc

To investigate the pore structure of the various $Fe_3O_4/FePc$ hybrid microspheres, nitrogen absorption and desorption experiments were carried out. N₂ absorption and desorption isotherms of *O*-Fe₃O₄/FePc and *E*-Fe₃O₄/FePc hybrid microspheres are shown in Figure 4a; they show a small hysteresis loop. The BET surface area and single point total pore volume of *O*-Fe₃O₄/FePc was calculated to be 34.6 m²/g and 0.101 cm³/g. In comparison, the BET surface area and single point total pore volume of hybrid microsphere was increased to 66.7 m²/g and 0.171 cm³/g. It indicates the obvious etching effects of hot NMP solvent on the Fe₃O₄/FePc hybrid microspheres. The pore size distribution of Fe₃O₄/FePc hybrid microsphere was calculated using the Barrett-Joyner-Halenda (BJH) model (desorption), and the results are shown in Figure 4b. It shows that the small peak of two lines at about 10–11 nm, and the BJH adsorption average pore diameter (4 V/A by BET) was 11.6 nm. The difference is that the pore volume of *E*-Fe₃O₄/FePc between 2 nm and 20 nm was much larger than that of *O*-Fe₃O₄/FePc. In summary, compared to the *O*-Fe₃O₄/FePc hybrid microsphere, the *E*-Fe₃O₄/FePc hybrid microsphere presented much more pore structures, which would result in a greater surface area.



Figure 4. (**a**) N₂ adsorption and desorption isotherms and (**b**) BJH isotherm curves (by adsorption) of *O*-Fe₃O₄/FePc and *E*-Fe₃O₄/FePc.

As reported, the nanoparticles would significantly affect the crystallization behavior of the crystallizable polymers. Especially, the interfacial interaction between the nanoparticles and the polymer matrix would directly influence the crystallization behavior. Thus, in order to further study the surface characteristics of the O-Fe₃O₄/FePc and E-Fe₃O₄/FePc hybrid microspheres, various Fe₃O₄/FePc microspheres with crystallizable PEN coated on the surfaces were prepared. The crystallization behaviors of the PEN on the surface of $Fe_3O_4/FePc$ were investigated with XRD and DSC. The results of the XRD are shown in Figure 5. It can be observed that the main diffraction peaks of *E*-Fe₃O₄/FePc at 30.1° (111), 35.5° (220), 43.0° (311), 53.5° (400), 57.1° (422), and 62.7° (511) are obvious and can clearly be assigned to Fe_3O_4 (JCPDS card no. 19–629). For the coated Fe_3O_4 /FePc, the characteristic diffraction peaks were all maintained and a new diffraction peak appeared at about 18° , which is attributed to the crystallization of PEN (shown in Figure 5b). In comparison, the peak at 18° for the c-PEN@E-Fe₃O₄/FePc is more obvious than that of c-PEN@O-Fe₃O₄/FePc. It indicates that the crystallization of PEN could be promoted by E-Fe₃O₄/FePc, and the promotion effects of E-Fe₃O₄/FePc were more obvious than that of O-Fe₃O₄/FePc. The obvious promotion effects of E-Fe₃O₄/FePc could be assigned to the fact that the larger surface areas offer more nucleation sites during the crystallization of *c*-PEN.



Figure 5. XRD curves of: (a) E-Fe₃O₄/FePc, (b) *c*-PEN@E-Fe₃O₄/FePc, and (c) *c*-PEN@O-Fe₃O₄/FePc, (d) pure PEN.

DSC was also used to investigate the effects of various Fe₃O₄/FePc hybrid microspheres on the crystallization of PEN. The DSC curves of the neat c-PEN, c-PEN@E-Fe₃O₄/FePc, and c-PEN@O-Fe₃O₄/FePc hybrid microspheres are shown in Figure 6a. From the DSC curves, we can clearly see the position of the glass transition and melting transition, and the glass transition temperature (T_g) of the curves are listed in Table 1. As observed, the T_gs decreased with the incorporation of Fe₃O₄/FePc hybrid microspheres. The T_g of neat c-PEN was 192.2 °C, and it declined to 189.7 °C with the introduction of O-Fe₃O₄/FePc. Moreover, the T_g of c-PEN@E-Fe₃O₄/FePc declined to 188.6 °C. This can be assigned to the fact that the micro/mesoporous structure of microspheres can offer more space for PEN segment vibration, so the PEN segments would move with a lower temperature [25], and the more micro/mesoporous structure, the more obvious this phenomenon. Meanwhile, we can see clearly from DSC curves that the melting peak intensity of *c*-PEN@*E*-Fe₃O₄/FePc was obviously higher than that of *c*-PEN@*O*-Fe₃O₄/FePc. The values of melting enthalpy are also collected in Table 1, with 8.90 and 6.87 J/g for c-PEN@E-Fe₃O₄/FePc and c-PEN@E-Fe₃O₄/FePc, respectively. The melting enthalpy of neat c-PEN was 22.16 J/g, where the *c*-PEN accounted for one-third of the mass of *c*-PEN@Fe₃O₄/FePc composite, so the theoretical melting enthalpy of c-PEN@Fe₃O₄/FePc composite was 7.39 J/g, which was between the value of *c*-PEN@*E*-Fe₃O₄/FePc and *c*-PEN@*E*-Fe₃O₄/FePc. It can them be claimed that the micro/mesoporous structure of E-Fe₃O₄/FePc can improve the crystallization degree of L-PEN.



Figure 6. (a) DSC and (b) TGA curves of neat *c*-PEN, *c*-PEN@*E*-Fe₃O₄/FePc, and *c*-PEN@*O*-Fe₃O₄/FePc after 4 h of heat treatment at 280 °C.

Samples	Neat <i>c</i> -PEN	<i>c</i> -PEN@O-Fe ₃ O ₄ /FePc	<i>c</i> -PEN@E-Fe ₃ O ₄ /FePc
T_g (°C)	192.2	189.7	188.6
ΔΗ̈́ (J/g)	22.16	6.87	8.90
$T_{5\%}$ (°C)	507.7	421.2	463.7

Table 1. The glass transition temperature (T_g) , melt enthalpy (ΔH), and initial decomposition temperature ($T_{5\%}$) of neat PEN, *c*-PEN@*E*-Fe₃O₄/FePc, and *c*-PEN@*O*-Fe₃O₄/FePc after 4 h of heat treatment at 280 °C.

The thermal stability of the neat *c*-PEN and its microspheres was obtained using a TGA measurement, and the results are shown in Figure 6b. The initial decomposition temperature ($T_{5\%}$) of each curve is listed in Table 1, which were 507.7 °C, 421.2 °C, and 463.7 °C for neat PEN, *c*-PEN@O-Fe₃O₄/FePc, and *c*-PEN@E-Fe₃O₄/FePc, respectively. The initial decomposition temperature of *c*-PEN@O-Fe₃O₄/FePc was the lowest because of the decomposition temperature of *c*-PEN@C-Fe₃O₄/FePc for *E*-Fe₃O₄/FePc, the initial decomposition temperature of *c*-PEN@E-Fe₃O₄/FePc increased by 10%. When the temperature was beyond 600 °C, the fast decomposition of curves can be attributed to the decomposition of Fe₃O₄ in the composites. In sum, due to the larger surface areas and the lower content of FePc, the *c*-PEN@E-Fe₃O₄/FePc hybrid microspheres possessed excellent thermal stability.

3.3. The Interfacial Characteristics and the Dielectric Properties of the Various Fe_3O_4 /FePc/H-PEN Composites

In order to study the interfacial interaction of the various $Fe_3O_4/FePc$ and high-performance PEN, the various $Fe_3O_4/FePc/H$ -PEN composites were prepared. The fracture surface of the composites was studied and is shown in Figure 7. Figure 7a-c compares the fracture surface SEM images of neat PEN, O-Fe₃O₄/FePc/H-PEN, and E-Fe₃O₄/FePc/H-PEN, which were obtained under the same conditions. It was found in Figure 7b,c that the hybrid microspheres were uniformly dispersed in the PEN matrix, and there was almost no hybrid microspheres agglomeration. Moreover, from the highlighted area with the arrow of the last two figures, we can see that there was no obvious gap between the hybrid microsphere and PEN matrix. This suggested a good interfacial compatibility between the PEN matrix and hybrid microspheres. As for the O-Fe₃O₄/FePc, the good interfacial compatibility was because of the surface organic component of O-Fe₃O₄/FePc having the similar structure and functional group with PEN chains. Different from O-Fe₃O₄/FePc, the surface organic components of E-Fe₃O₄/FePc were etched by NMP, and the good interfacial compatibility was mainly due to the large number of micro/mesoporous structures of E-Fe₃O₄/FePc. PEN chains could enter or even penetrate these micro/mesoporous regions, so that the PEN chains could intertwine with these micro/mesoporous structure microspheres. The difference is that the interfacial adhesion between the etched hybrid microsphere and PEN matrix was slightly inferior between the original hybrid microspheres and PEN matrix. This was because the pore size and distribution of micro/mesoporous regions on the surface of the E-Fe₃O₄/FePc were inhomogeneous, and in some areas, the PEN chains could not enter the channel of pores. In sum, it can be concluded that organic component of hybrid microsphere surface and micro/mesoporous structures of microspheres can improve the interfacial compatibility between microspheres and matrix.



Figure 7. The fracture surface SEM image of (**a**) neat PEN, (**b**) O-Fe₃O₄/FePc/H-PEN, and (**c**) E-Fe₃O₄/FePc/H-PEN.

The dielectric properties of H-PEN hybrid microsphere composite films are shown in Figure 8a-c. Figure 8a,b presents the dielectric constant and dielectric loss curves of neat PEN, O-Fe₃O₄/FePc/*H*-PEN, and *E*-Fe₃O₄/FePc/*H*-PEN with the change of frequency. From 100 Hz to 200 kHz, the dielectric constant of neat PEN film and PEN hybrid microsphere composite films decreased slightly with the increase in test frequency. Furthermore, with the addition of hybrid microspheres, the dielectric constant of PEN composite films increased at the same frequency. The dielectric constant of E-Fe₃O₄/FePc/H-PEN was higher than the value of O-Fe₃O₄/FePc/H-PEN. This was mainly due to the following two factors: (1) the Fe₃O₄/FePc hybrid microsphere possessed a high dielectric constant, and (2) the high surface area of E-Fe₃O₄/FePc increased the interface polarization between the filler and polymeric matrix. The same tendency was found for the dielectric loss of neat PEN film and PEN hybrid microsphere composite films. The dielectric loss of these films exhibited obvious frequency dependence, where a dramatic decrease was observed at low frequency, and then it increased slightly after the frequency reached 10 kHz. Nevertheless, the dielectric loss was still within a low range, with a fluctuation range of 0.015–0.026. Figure 8c shows the breakdown strength of neat PEN, O-Fe₃O₄/FePc/H-PEN, and E-Fe₃O₄/FePc/H-PEN. Compared with the neat PEN film (206 kV/mm), the addition of 3 wt% O-Fe₃O₄/FePc and E-Fe₃O₄/FePc into the PEN matrix reduced the breakdown strength, which was decreased by 9.7% and 18.6%, respectively. That was because the introduction of Fe₃O₄/FePc hybrid microspheres introduced some defects, which led to a reduction in the breakdown strength [26]. Furthermore, the E-Fe₃O₄/FePc, having a high surface area, possessed more micro/mesoporous regions, which introduced more defects compared with O-Fe₃O₄/FePc with the same content.

Figure 8d shows the tensile strength and tensile modulus of neat PEN film and PEN $Fe_3O_4/FePc$ hybrid microsphere composite films. As can be seen, with the addition of $Fe_3O_4/FePc$ hybrid microspheres (3%), the tensile strength and tensile modulus increased slightly. The $E-Fe_3O_4/FePc/H$ -PEN exhibited a higher value of tensile strength and tensile modulus compared with $O-Fe_3O_4/FePc/H$ -PEN. This might be attributed to the entanglement effect of PEN molecules on the micro/mesoporous structure microsphere. Compared with traditional inorganic filler SiO₂, the tensile strength of $E-Fe_3O_4/FePc/H$ -PEN composite films (101.5 MPa with 3 wt% padding) was obviously higher than for SiO₂/PEN composite films (92.3 MPa with 3 wt% padding) with similar content. At low filler content, the tensile strength of composite films decreased with the introduction of SiO₂, which was different from $Fe_3O_4/FePc/H$ -PEN composite films [27]. These results can also indicate the organic component of hybrid microsphere surface and micro/mesoporous structure of hybrid microsphere can improve the interfacial compatibility between microspheres and the polymeric matrix.





Figure 8. The (**a**) dielectric constant, (**b**) dielectric loss, (**c**) breakdown strength, and (**d**) mechanical property of neat *H*-PEN film, A: O-Fe₃O₄/FePc/*H*-PEN and B: *E*-Fe₃O₄/FePc/*H*-PEN.

4. Conclusions

In this study, a novel micro/mesoporous structure of Fe₃O₄/FePc hybrid microspheres were successfully prepared using a simple solvothermal method and solution etching. SEM, TEM, and SPM images and curves of the adsorption and desorption isotherms of N₂ confirmed that the *E*-Fe₃O₄/FePc presented much more micro/mesoporous structure than that of *O*-Fe₃O₄/FePc. The BET surface area and single point total pore volumes of *E*-Fe₃O₄/FePc were 66.7 m²/g and 0.171 cm³/g, respectively. The crystallization of crystallizable PEN could be improved with the introduction of *E*-Fe₃O₄/FePc. Moreover, the organic component of the hybrid microsphere surface and micro/mesoporous structure of hybrid microspheres can improve the interfacial compatibility between microspheres and polymeric matrix, which was confirmed with the investigation of the fracture surface morphology and mechanical properties of the composite films. Meanwhile, the incorporation of *E*-Fe₃O₄/FePc increased the dielectric property and mechanical property of composite films. Therefore, these excellent properties make the micro/mesoporous hybrid microspheres a good candidate in the applications of high-performance composites.

Supplementary Materials: The following are available online at http://www.mdpi.com/1996-1944/11/8/1356/ s1, Figure S1: Digital photo of NMP solution (1) before etching and (2) after etching, Figure S2: The UV-vis spectra NMP solution after etching and the controlled sample of TPH and FePc in the NMP solution, Figure S3: TGA curves of the Fe₃O₄/FePc hybrid microspheres before and after etching.

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