Preparation and Enhanced Properties of Fe₃O₄ Nanoparticles Reinforced Polyimide Nanocomposites

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Abstract

Polyimide (PI) nanocomposite reinforced with Fe_3O_4 nanoparticles (NPs) at various NPs loadings levels of 5.0, 10.0, 15.0, and 20.0 wt% were prepared. The chemical interactions of the Fe_3O_4 NPs/PI nanocomposites were characterized using Fourier Transform Infrared (FT-IR) spectroscopy. X-ray Diffraction (XRD) results revealed that the addition of NPs had a significant effect on the crystallization of PI. Scanning electron microscope (SEM) and the atomic force microscope (AFM) were used to characterize the dispersion and surface morphology of the Fe_3O_4 NPs and the PI nanocomposites. The obtained optical band gap of the nanocomposites characterized using Ultraviolet–Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS) was decreased with increasing the Fe_3O_4 loading. Differential scanning calorimetry (DSC) results showed a continuous increase of T_g with increasing the Fe_3O_4 NPs loading. Some differences were observed in the onset decomposition temperature between the pure PI and nanocomposites since the NPs and the PI matrix were physically entangled together to form the nanocomposites. The contact angle of pure PI was larger than that of Fe_3O_4 /PI nanocomposites films, and increased with increasing the loading of Fe_3O_4 . The degree of swelling was increased with increasing the Fe_3O_4 loading and the swelling time. The dielectric properties of the nanocomposite were strongly related to the Fe_3O_4 loading levels. The Fe_3O_4 /PI magnetic property also had been improved with increasing the loading of the magnetic nanoparticles.

Keywords: Polyimide; Fe_3O_4 ; magnetic properties; mechanical properties; optical properties; dielectric properties

1. Introduction

Polymer nanocomposites (PNCs) or inorganic–organic hybrid materials have attracted both academic and industrial attentions during the last few decades due to their extraordinary properties because of the property synergism among the components, and the potential wide applications.[1-6] These materials have gained great interests due to the remarkable improvement in properties such as mechanical,[7] magnetic,[8] optical,[9-11] thermal and electrical,[12, 13] compared to pure polymers or conventional micron- and macro- composites. Traditionally, polymer matrix was filled with natural or synthetic inorganic compounds in order to improve their properties. Typically the nanofillers can be divided based on their basic physical structures as particles, fibers or plates. Polyimide (PI), a class of thermal stable polymers, is well known and widely used in different fields of industries for their extremely high thermal and chemical stability and excellent electrical and mechanical properties.[14-16] For example, cobalt-containing PI has been studied and applied for moisture sensing and absorption.[17] The well-dispersed hexagonal boron nitride (h-BN) composite films with oriented cross-linked liquid crystalline (LC) polyimide were obtained as high thermally conductive materials.[18] The PI has been used to fabricate pervaporation membranes for the separation of ethanol/water mixtures.[19] The well-dispersed single-walled and multiple-walled carbon nanotubes functionalized with polyimide derivatives were obtained.[20] Soluble polyimide containing benzimidazole rings synthesized via one-pot synthetic method have been studied for inter-level dielectrics.[21] The control of the composite layer microstructure was achieved by embedding nickel NPs in the

polyimide matrix to catalyze the hydrogenation and decomposition.[22] A wide variety of other NPS such as polyhedral oligomeric silsesquioxane (POSS),[23] silica,[24] copper,[25] and TiO_2 [26] has also been introduced to the PI matrix to obtain various unique properties.

During the past decades, magnetic nanoparticles have attracted long-standing interest owing to their unique properties and potential applications. In particular, Fe_3O_4 NPs, an important member of spinel type ferrite, have extensive applications not only in the field of magnetic recording but also in the areas of ferrofluid,[27, 28] magnetoresistance sensing,[29] drug delivery,[30, 31] bifunctional materials,[32, 33] mineral separation,[34, 35] and efficient heat transfer applications.[36] The Fe_3O_4 NPs have also been applied to form diversified core/shell nanoparticles with other materials such as FePt,[37] Au,[38] Ag[39] and FeO.[40] All of these applications are attributed to their extraordinary physical and chemical properties, including high specific surface area, low toxicity, superparamagnetic activities, and simple separation by an external magnet. However, the method of incorporating Fe_3O_4 NPs to fabricate PI nanocomposites with magnetic properties is rarely reported so far.

In this work, the Fe_3O_4 NPs/PI nanocomposites with various Fe_3O_4 nanoparticle loadings (5, 10, 15, and 20 wt%) were fabricated. The chemical structures of the Fe_3O_4 NPs/PI nanocomposites were characterized. Scanning electron microscope (SEM) and atomic force microscope (AFM) were used to characterize the dispersion and the surface morphology of the Fe_3O_4 NPs, and Fe_3O_4 NPs/PI nanocomposites. The optical properties were characterized by ultraviolet–visible diffuse reflectance spectroscopy (UV-Vis DRS). The magnetic properties of

the nanocomposites were investigated and a Physical Properties Measurement System (PPMS) by Quantum Design. The effects of Fe₃O₄ NPs on the crystallization of PI were studied by X-ray diffraction (XRD). The thermal stability of the nanocomposites compared with pure PI was assessed by differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA). The dielectric properties and mechanical properties of the nanocomposite films were characterized by LCR meter and tensile test, respectively. The contact angles and degree of swelling of the nanocomposite films were also tested.

2. Experimental section

2.1. Materials

Polyimide (PI, powder, Matrimid 5218 US) was provided by Huntsman Advanced Materials Americas, Inc. Scheme 1 shows the molecular structure of PI. *N,N*-Dimethylformamide (DMF, 99.9%, anhydrous) was purchased from Fisher Scientific Inc. The Fe₃O₄ NPs with an average size of 20 nm were obtained from Nanjing Emperor Nano Material Co., Ltd., China. The Fe₃O₄ nanoparticles were dried at 140 °C to remove residual water.

Scheme 1: Molecular structure of polyimide (Matrimid 5218 US)

2.2. Preparation of Polyimide and Nanocomposite Solutions

The PI/DMF polymer solutions with a PI loading of 8.0, 10.0, 15.0 and 20.0 wt% were prepared by mechanical stirring (200 rpm) overnight at room temperature to completely dissolve the polymer. The nanocomposite solutions were prepared from 8.0% PI/DMF solution. The Fe₃O₄ NPs (5.0, 10.0, 15.0, and 20.0 wt% , with regard to the weight of PI) were added into the polymer solution, respectively. After completely wetting the Fe₃O₄ NPs with the polymer solution, both mechanical stirring (300 rpm) and ultra-sonication were simultaneously applied for 30 minutes to fully disperse the NPs in PI/DMF solution. Pure PI and Fe₃O₄ NPs/PI nanocomposite solutions were both used for casting films. All the experiments were performed at room temperature.

2.3. Fabrication of Pristine PI and Nanocomposites Films

Pure PI and Fe₃O₄ NPs/PI nanocomposite films were prepared by casting viscous polymer solutions on a horizontal glass mold. Then the films were dried at 80 °C in a vacuum oven for 12 h to remove solvent. Finally the films were dried at 140 °C under vacuum for 48 h to remove the residual solvent and stored for further characterization.

2.4. Characterization

Fourier transform infrared spectroscopy (FT-IR) characterization of pure PI and its nanocomposite films was performed on a FT-IR spectrometer coupled with an ATR accessory (Bruker Inc. Vector 22) in the range from 500 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹. X-ray diffraction (XRD) analysis was conducted on a Bruker AXS D8 Discover diffractometer with

General Area Detector Diffraction System (GADDS) operating with a Cu-K α radiation source filtered with a graphite monochromator ($\lambda = 1.5406 \text{ \AA}$). The data were collected at scanning rate of 4° min^{-1} in a range of 5 to 80° . The morphology of pure PI and Fe₃O₄/PI nanocomposite films was characterized by scanning electron microscopy (SEM, Hitachi S-3400) and atomic force microscopy (AFM, Agilent 5600 system with multipurpose 90 mm scanner). The mechanical properties of pure PI and its Fe₃O₄ nanocomposite films were characterized by tensile test. The glass transition temperature (T_g) was measured with differential scanning calorimetry (DSC, TA Instruments). The T_g of the samples was determined as the midpoint temperature of the transition region in the second heating cycle. The DSC heat flow and temperature were calibrated with an indium standard. The thermal stability was investigated with a thermo gravimetric analysis (TGA Q-500, TA Instruments). The TGA was conducted on pure PI and its Fe₃O₄ nanocomposite films in the temperature range of 30-900 $^\circ\text{C}$ with a heating rate of 10 $^\circ\text{C}/\text{min}$ and a nitrogen flow rate of 60 mL/min. The magnetic properties tests were carried out at room temperature in a 9 T Physical Properties Measurement System (PPMS) by Quantum Design. The dielectric properties were investigated by a LCR meter (Agilent, E4980A) equipped with a dielectric test fixture (Agilent, 16451B) at the frequency ranging from 20 to 2×10^6 Hz at room temperature. The contact angles were measured by the sessile drop method with a contact angle analyzer (Contact angle analyzer, Future Digital Scientific Corp.). Pure PI and its Fe₃O₄ nanocomposite films were immersed in n-Hexadecane at 50 $^\circ\text{C}$ for the swelling test. The degree of swelling of films was measured after 4, 8, 12, 16, 20, 24, 48, and 72 hours.

3. Results and Discussion

3.1. Microstructure of the $\text{Fe}_3\text{O}_4/\text{PI}$ Nanocomposites Films (SEM/AFM)

Fig. 1 SEM images of pure PI and $\text{Fe}_3\text{O}_4/\text{PI}$ nanocomposites films with a Fe_3O_4 nanoparticle loading of (a) 0.0, (b) 5.0, (c) 10.0, (d) 15.0, (e) 20.0 and (f) 100.0 wt%.

Fig. 2 SEM images of the cross-section of pure PI and $\text{Fe}_3\text{O}_4/\text{PI}$ nanocomposites films with a Fe_3O_4 nanoparticle loading of (a) 0.0, (b) 5.0, (c) 10.0, (d) 15.0, and (e) 20.0 wt%.

The major issues occurred during the fabrication of matrix films were the surface effect, physical properties of the polymer, particle agglomeration and polymer/particle interactions.[41] Fig. 1 and Fig. 2 show the SEM micrographs of the surface and the cross-section of the nanocomposite films with different nanoparticle loadings, respectively. These indicate that the Fe₃O₄ NPs are uniformly distributed in the films surface and cross-section. Fig. 1(d) shows slight agglomeration of the nanoparticles as the particle loading is increased to 15.0 wt%. The agglomeration was attributed to the magnetic dipole–dipole interactions (also called the dipolar coupling, direct interaction between two magnetic dipoles) between the Fe₃O₄ NPs.[42] The cross-section SEM images of the Fe₃O₄/PI nanocomposite films show that the contact between the polymer matrix and the nanofillers was improved. The results also demonstrated a uniform distribution of the Fe₃O₄ NPs in PI. To some degree, the surface of nanocomposite films is not as smooth as that of pure PI films since the motion of polymer chains was restricted by the introduced nanoparticles. Under such circumstances, the polymer chains were less patterned than pure PI and thus showed a rougher surface.[43]

3.2. FT-IR Analysis

Fig. 3 shows the FT-IR spectra of pure PI and its Fe₃O₄ nanocomposite films. The absorption band at 2959 cm⁻¹ was assigned to the aromatic C–H stretch of methyl groups. The bands shown at 1782 and 1716 cm⁻¹ were attributed to the symmetric and asymmetric stretching of the C=O in the imide group, respectively. The benzophenone C=O stretching was observed at 1668 cm⁻¹. The bands at 1506 and 1482 cm⁻¹ were assigned to the aromatic stretching of the

para-disubstituted phenyl group. The 1361 and 1086 cm^{-1} absorption bands were attributed to the stretching of the C–N–C of the imide 5-membered ring.[44] The 1,2,4-trisubstitute of the benzene structure was observed at 864, 827, and 714 cm^{-1} . [43] Compared to the FT-IR spectrum of pure PI, no additional bands were observed in the spectra of $\text{Fe}_3\text{O}_4/\text{PI}$ nanocomposite films. All the observed bands in the FT-IR spectra confirmed that the molecular structure of PI was well maintained after dissolving in DMF and being casted into films. This indicates that the nanoparticles and PI matrix were physically entangled together to form the nanocomposites, rather than form chemical bonding.

Fig. 3 FT-IR spectra of pure PI and its Fe_3O_4 nanocomposite films with a Fe_3O_4 nanoparticle loading of (a) 0.0, (b) 5.0, (c) 10.0 (d) 15.0, and (e) 20.0 wt%.

3.3. XRD Analysis

Fig. 4 shows the XRD patterns of pure PI, Fe₃O₄ NPs, and the Fe₃O₄/PI nanocomposites films with different Fe₃O₄ nanoparticle loadings. For pure PI, only a very broad peak was observed in the range $2\theta = 15-22^\circ$ and this wide peak was due to a polyimide amorphous phase.[45] This broad peak was diminished as the Fe₃O₄ NPs loading increased because of the reduced proportion of the amorphous PI presented. Meanwhile, in the Fe₃O₄/PI nanocomposites films, the diffraction peaks of Fe₃O₄ can be observed at $2\theta=35, 43$ and 62° , and become more notable with increasing the Fe₃O₄ nanoparticle loading. These peaks are assigned to the corresponding (3-1-1), (4-0-0) and (4-4-0) planes of crystalline Fe₃O₄, respectively.[46] The d spacing value of all the samples can be calculated using Bragg's Law[47]. The PI peak was located at $2\theta=15.65.68^\circ$. The average grain size (L) is estimated from the Debye-Scherrer Equation, as shown in Equation (1):[48]

$$L = \frac{\kappa \lambda}{\beta \cos \theta} \quad (1)$$

where the constant κ is 0.94, β is the full width of the peak at half maximum height (FWHM), λ is the wavelength of Cu-K α radiation, and L is the average diameter of the crystallite. The peak at $2\theta=35^\circ$ is used to estimate the particle size. The calculated values are about 8.7, 6.1, 5.7 and 7.1 nm for the different NPs loadings from 5.0-20.0 wt%.

Fig. 4 XRD patterns of pure PI and $\text{Fe}_3\text{O}_4/\text{PI}$ nanocomposites films with different Fe_3O_4 nanoparticle loadings: (a) 0.0, (b) 5.0 (c) 10.0, (d) 15.0, and (e) 20.0 wt%.

3.4. Optical Properties (UV-Vis)

Fig. 5 UV-Vis diffuse reflectance spectra of pure PI, pure Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{PI}$ nanocomposite films with a Fe_3O_4 nanoparticle loading of (a) 0.0, (b) 5.0 (c) 10.0 (d) 15.0 (e) 20.0 and (f) 100 wt%.

The optical property is an important aspect to be considered for the applications of materials in electronic devices[49, 50] and photo catalysis.[51, 52] Ultraviolet-Visible diffuse reflectance spectroscopy (UV-Vis DRS) has been widely used for the measurement of the UV-Vis absorption edge (λ_{edge} , the transition between strong short-wavelength and weak long-wavelength absorption in the spectrum of a solid sample).[53] The spectral position of this absorption edge is determined by the energy difference between the valence state and the conduction state. The band gap (E_g^{opt}) can be obtained from Equation (2) based on the onset of UV-Vis diffuse reflectance spectra of the samples:[54]

$$E_g^{\text{opt}} (\text{eV}) = 1240 / \lambda_{\text{edge}} (\text{nm}) \quad (2)$$

where E_g^{opt} is the optical band gap (difference between the valence band and the conduction band) and the number 1240 is obtained from the relationship between frequency and wavelength as described following Equation (3):[42]

$$E(\text{eV}) = h\nu = hc / \lambda \quad (3)$$

where h is Planck's constant, c is the speed of light in a vacuum and e is the electron charge, the unit of λ is meter, and then 1240 can be obtained from hc .

Table 1 Absorption edge and optical band gap of pure PI and Fe₃O₄/PI nanocomposite films with a Fe₃O₄ nanoparticle loading of 5.0%, 10.0%, 15.0%, and 20.0%

Samples with different Fe ₃ O ₄ NPs loadings	Absorption edge of PI ($\lambda_{\text{edge, nm}}$)	Optical band gap of PI ($E_{\text{g}}^{\text{opt}}$, eV)
0.0%	447	2.77
5.0%	443	2.80
10.0 %	458	2.70
15.0 %	470	2.64
20.0 %	472	2.62

Fig. 5 shows the UV-Vis diffused reflectance spectra of pure PI and its Fe₃O₄ nanocomposite films with different Fe₃O₄ loadings. According to Equation (2), the λ_{edge} of pure PI calculated by the onset of the UV-Vis DRS in Fig. 4 was 447 nm and the $E_{\text{g}}^{\text{opt}}$ of pure PI was 2.77 eV. The calculated $E_{\text{g}}^{\text{opt}}$ of pure PI was consistent with the results investigated previously in the PI (λ_{edge} is in 400 – 550 nm)[55] and in the pure PI.[56] And this was attributed to the transition of electron from π to π^* in the phenyl ring.[57] The λ_{edge} and the corresponding calculated $E_{\text{g}}^{\text{opt}}$ for the Fe₃O₄/PI nanocomposites films with a Fe₃O₄ nanoparticle loading of 5.0, 10.0, 15.0 and 20.0 wt% obtained from UV-Vis DRS are listed in Table 1. From Table 1, the band gap of PI decreases with increasing the Fe₃O₄ loading, which was due to the interaction between Fe₃O₄ NPs and PI polymer backbone.

3.5. DSC Analysis

Fig. 6 DSC thermograms of pure PI and its Fe_3O_4 nanocomposites films with a Fe_3O_4 nanoparticle loading of (a) 0.0, (b) 5.0, and (c) 20.0 wt%.

The glass transition temperature (T_g) of the films was measured with differential scanning calorimetry (DSC, TA Instruments). The film samples were cut into small pieces, weighed and placed into a T_{zero} Pan (TA Instruments). The weight of each sample was about 5-10 mg. Then, the sample was heated from 25 to 350 °C with a nitrogen flow rate of 20 mL/min and a heating rate of 10 °C/min in the first cycle to remove the thermal history. Then, the sample was naturally cooled down to 40 °C and heated again to 350 °C with the same conditions as the first scan. The

T_g of the sample was determined as the midpoint temperature of the transition region in the second heating cycle. Fig. 6 shows the DSC curves of pure PI and its Fe_3O_4 nanocomposites films. The dip observed at around 320 °C indicates the glass transition temperature. It is evident that T_g was slightly increased with increasing the Fe_3O_4 nanoparticle loading. The T_g for pure PI was 319.37 °C and increased to 320.44 °C for the nanocomposites containing 5.0 wt% Fe_3O_4 NPs and further to 320.74 °C for the nanocomposites containing 20.0 wt% Fe_3O_4 NPs. The observed T_g of pure PI was consistent with the results investigated previously in the mixed matrix membranes for O_2/N_2 gas separation (T_g of pure PI is 320 °C).^[58] A similar phenomenon was observed in polymer/clay nanocomposites, where the DSC results showed a continuous increase in T_g with the addition of the Fe_3O_4 content.^[59] The increase in T_g observed in the PI nanocomposites with increasing the nanoparticle loading was attributed to the interactions between Fe_3O_4 NPs, PI matrix and the confinement of PI polymer chains, which restricted the segmental motions of the polymer chains at the organic-inorganic interface.^[60]

3.6. Thermo Gravimetric Analysis (TGA)

The thermal stability of pure PI and its Fe_3O_4 nanocomposite films with different Fe_3O_4 loadings was studied by thermo gravimetric analysis. Fig. 7 shows the weight percentage change of the material as a function of temperature. Table 2 shows the summarized thermal properties of pure PI and its Fe_3O_4 nanocomposites films. For all the nanocomposites, there is only one main degradation (weight loss) stage associated with the breaking of the cross-linked network in

polymer and the release of moisture and organic solvent residue entangled in the PI polymer chains.[61] From the onset decomposition temperature summarized in Table 2, the decomposition temperature was firstly increased with increasing the Fe_3O_4 nanoparticle loading (5.0, 10.0 and 15.0 wt%), then decreased (20.0 wt%) but still lower than that of pure PI. The enhanced thermal stability is associated with the protection effect of the Fe_3O_4 NPs, which could act as a shield and separate the polymer chains from heat.[61] The temperatures to reach 10% ($T_{d10\%}$) and 15% ($T_{d15\%}$) weight loss (only refers to the PI fraction of the nanocomposite films since the Fe_3O_4 does not decompose) in TGA tests were usually reported to characterize the thermal stability of a material. The $T_{d10\%}$ and $T_{d15\%}$ for pure PI and its Fe_3O_4 nanocomposites films with a Fe_3O_4 nanoparticle loading of 5.0, 10.0, 15.0 and 20.0 wt% were also summarized in Table 2. The weight residues of the $\text{Fe}_3\text{O}_4/\text{PI}$ nanocomposites with an initial Fe_3O_4 nanoparticle loading of 5.0, 10.0, 15.0 and 20.0 wt% at 400 °C were 94.6, 92.8, 95.4 and 96.1 wt%, respectively. The weight residues of the $\text{Fe}_3\text{O}_4/\text{PI}$ nanocomposites with an initial Fe_3O_4 nanoparticle loading of 5.0, 10.0, 15.0 and 20.0 wt% at 800 °C were 53.9, 52.9, 54.7 and 53.6 wt%. The thermal stability of PI in the temperature range of 300-400 °C demonstrated the capability to process these nanocomposites within this temperature range.[43] Some differences were observed in the onset decomposition temperature between pure PI and the composites. This indicates that the Fe_3O_4 NPs have some positive influences on the thermal stability of the nanocomposites, and the nanoparticles and PI matrix are physically entangled together to form the nanocomposites.

Fig. 7 TGA curves under nitrogen of pure PI and its Fe_3O_4 nanocomposite films with a Fe_3O_4 nanoparticle loading of (a) 0.0, (b) 5.0, (c) 10.0, (d) 15.0, and (e) 20.0 wt%.

Table 2 Thermal properties of pure PI and its Fe_3O_4 nanocomposite films with a Fe_3O_4 nanoparticle loading of 5.0, 10.0, 15.0, and 20.0 wt%.

Samples with different NPs loadings (wt%)	Onset temperature (°C)	10 wt% loss decomposition temperature (°C)	15 wt% loss decomposition temperature (°C)	Weight residue (wt%) at 400 °C	Weight residue (wt%) at 800 °C
0.0	502.26	504.5	517.1	93.9	53.1
5.0	488.82	494.8	506.5	94.6	53.9
10.0	489.19	488.5	503.9	92.8	52.9
15.0	495.57	505.2	517.8	95.4	54.7
20.0	486.81	498.9	511.4	96.1	53.6

3.7. Contact Angle

The contact angles of pure PI and its Fe_3O_4 nanocomposite films with different Fe_3O_4 nanoparticle loadings were measured by the sessile drop method with a contact angle analyzer (SEO 300A by Surface Electro Optics Corporation Ltd., Korea). A total of 3 μl drops of deionized (DI) water was carefully placed on the substrate using a microliter syringe. The drop was viewed using a CCD camera attached to a microscope, and the drop image was digitized and stored in a computer every second during the measurement. The contact angles of each drop were measured five times to obtain an average value. The shape of the drop on the surface did not change significantly during the measurement. All measurements were carried out at room temperature.

Fig. 8 Contact angle of the $\text{Fe}_3\text{O}_4/\text{PI}$ nanocomposite films with a Fe_3O_4 loading of (a) 0.0, (b) 5.0, (c) 10.0, (d) 15.0, and (e) 20.0 wt%.

Hydrophilicity of pure PI and its Fe₃O₄ nanocomposites films with different Fe₃O₄ loadings is shown in Fig. 8 and summarized in Table 3. The contact angle of pure PI and its Fe₃O₄ nanocomposites with an initial Fe₃O₄ nanoparticle loading of 0.0, 5.0, 10.0, 15.0 and 20.0 wt% were 100.5, 90.9, 93.6, 96.1 and 99.2°, respectively. It is obvious that the contact angle of pure PI was bigger than that of the Fe₃O₄/PI nanocomposites films, indicating that the increase in the roughness reduced the contact angles.[62] The decrease of the contact angle was mainly attributed to the increase in the total surface energy of the PI films due to the increased specific surface area induced by roughening.[63] Besides, the contact angle of the Fe₃O₄/PI nanocomposites films increased with increasing the loading of Fe₃O₄. The hydrophilicity of PI films was reduced due to the presence of more Fe₃O₄ nanoparticles on the film surface. More magnetic nanoparticle attachment leads to a higher contact angles. This could be due to the relative hydrophobicity of the nanoparticle surface. A similar result was reported for the magnetic field responsive nanofiltration membranes.[64]

Table 3 Contact angles of pure PI and Fe₃O₄/PI nanocomposite films with a Fe₃O₄ nanoparticle loading of 5.0%, 10.0%, 15.0%, and 20.0%

Samples with different Fe ₃ O ₄ NPs loadings (wt%)	Contact angle (°)
0.0	100.5
5.0	90.9
10.0	93.6
15.0	96.1
20.0	99.2

3.8. Dielectric Properties

Fig. 9 (a) Real permittivity (ϵ'), (b) imaginary permittivity (ϵ'') and (c) dielectric loss ($\tan \delta$, where $\tan \delta = \epsilon'' / \epsilon'$) as a function of frequency for pure PI and its Fe_3O_4 nanocomposite films within the frequency range of 20 to 2×10^6 Hz at room temperature.

Fig. 9 shows the real permittivity (ϵ' , Fig. 9(a)), imaginary permittivity (ϵ'' , Fig. 9(b)), and dielectric loss tangent ($\tan \delta$, where $\tan \delta = \epsilon'' / \epsilon'$, Fig. 9(c)) as a function of frequency at room temperature for pure PI and its Fe_3O_4 nanocomposite films with a Fe_3O_4 nanoparticle loading of 5.0, 10.0, 15.0, and 20.0 wt%. In Fig. 9(a), all these samples exhibited positive real permittivity within the measured frequency range and the ϵ' was decreased with increasing the frequency from 10^2 to 10^6 Hz. The decrease of ϵ' at high frequency was attributed to the dipolar groups, which cannot follow the speed of the alternating electric field (dielectric relaxation phenomena).[61] The inset of Fig. 9(a) shows the positive ϵ' value within the frequency range from 10^4 to 10^6 Hz. Generally, the frequency-dependent dielectric properties of the nanocomposites are strongly related to the interfacial polarization between the hosting polymer matrix and the nanoparticles. This phenomenon is called as the Maxwell - Wagner - Sillars

(MWS) polarization effect, in which the charge carriers are accumulated at the inner dielectric boundary layers or at the interfaces within composites matrix.[54, 65] The $\text{Fe}_3\text{O}_4/\text{PI}$ nanocomposite films with a Fe_3O_4 nanoparticle loading of 20.0 wt% had the highest value of ϵ' compared with other.

Fig 9(b) shows the ϵ'' of pure PI and its Fe_3O_4 nanocomposites films with a Fe_3O_4 nanoparticle loading of 5.0, 10.0, 15.0, and 20.0 wt%. The ϵ'' of pure PI was decreased with increasing the frequency at low frequency ranges ($<10^4$ Hz), then increased after 10^4 Hz. The ϵ'' of the $\text{Fe}_3\text{O}_4/\text{PI}$ nanocomposites with a Fe_3O_4 nanoparticle loading of 10.0 and 20.0 wt% exhibited a similar decrease then increase trend as that of pure PI. The ϵ'' value of the 15.0 wt% $\text{Fe}_3\text{O}_4/\text{PI}$ nanocomposites was increased monotonically with increasing the frequency from 10^2 to 10^6 Hz. However the ϵ'' value of the 5.0% $\text{Fe}_3\text{O}_4/\text{PI}$ nanocomposites was increased and then decreased at low frequency range ($<10^4$ Hz), then increased at high frequency range ($>10^4$ Hz).

Fig. 9(c) shows the frequency-dependent $\tan \delta$ for pure PI and its Fe_3O_4 nanocomposites films with a Fe_3O_4 nanoparticle loading of 5.0, 10.0, 15.0, and 20.0 wt%. The $\tan \delta$ patterns for different loading nanocomposites were similar to the ϵ'' pattern for different loading nanocomposites. And $\tan \delta$ was increased monotonically after 10^4 Hz with increasing the frequency. The observed higher $\tan \delta$ of the nanocomposites than that of pure PI is related to the free charge motion difference, indicating that there was an interfacial polarization in the nanocomposites.[61] The composites with low energy loss have a potential application in the microelectronic devices.

3.9. Magnetic Property

Fig. 10 Room temperature hysteresis loops of the Fe₃O₄/PI nanocomposite films with a Fe₃O₄ nanoparticle loading of (a) 0.0, (b) 5.0, (c) 10.0, (d) 15.0, and (e) 20.0 wt%. Inset shows the hysteresis loop of pure nanoparticles.

Fig.10 shows the room temperature magnetic hysteresis loops of Fe₃O₄/PI nanocomposite films with a Fe₃O₄ nanoparticle loading of 5.0, 10.0, 15.0, and 20.0 wt%. The insert of Fig. 10 shows the hysteresis loop of the as-received pure Fe₃O₄ NPs. The saturation magnetization (M_s) is defined as the state, at which point the magnetic field cannot increase the magnetization of the material further.[66] The pure PI was observed to be non-magnetic as expected, whereas the curves of the others showed no hysteresis loops. The M_s of the as-received Fe₃O₄ NPs was not reached even at high magnetic field and was determined by the extrapolated saturation

magnetization obtained from the intercept of $M \approx H^{-1}$ at high field.[67] The Fe_3O_4 NPs did not show hysteresis loop with zero coercivity, indicating the superparamagnetic behavior at room temperature. The calculated M_s of the as-received Fe_3O_4 NPs was 58.09 emu g^{-1} . The M_s values of the PI/ Fe_3O_4 films with a particle loading of 5, 10, 15 and 20 wt% were observed to be saturated at a lower field and were 1.96, 2.72, 4.43 and 5.21 emu g^{-1} , respectively. The M_s of the PI/ Fe_3O_4 films was increased with increasing the Fe_3O_4 NPs loading, which is due to the increased proportion of the magnetic particles. In addition, the magnetization was saturated more rapidly in the PI/ Fe_3O_4 films with a lower NP loading. An infinitesimal coercivity was observed in all the samples, indicating a superparamagnetic behavior of the NPs disregard of the polymer matrix.[68]

3.10. Swelling Property

Pure PI and its nanocomposites films were dried under vacuum at 140°C for 48 h and pre-weighed, then immersed in n-hexadecane for the swelling test. Each dried film was swollen in n-hexadecane at 50°C to achieve equilibrium swelling. The degree of swelling of films was measured after 4, 8, 12, 16, 20, 24, 48 and 72 hours. The swollen sample was taken out and immediately weighed after drying the samples with tissue papers. The degree of swelling was calculated from the difference between the wet weight after sorption equilibrium and the original dry weight.[69]

Fig. 11 shows the degree of swelling of Fe_3O_4 /PI nanocomposites films with different Fe_3O_4

NPs loadings. The degree of swelling of the $\text{Fe}_3\text{O}_4/\text{PI}$ nanocomposites films was increased with increasing the Fe_3O_4 loading and swelling time. This can be explained by the physical entanglement of the NPs in between the PI matrix. As increasing the Fe_3O_4 loading, the NPs involved in the PI matrix were agglomerated strongly than lower loadings, and the degree of swelling started to increase.

Fig.11 Degree of swelling of $\text{Fe}_3\text{O}_4/\text{PI}$ nanocomposite films with a Fe_3O_4 nanoparticle loading of (a) 0.0, (b) 5.0, (c) 10.0, (d) 15.0, and (e) 20.0 wt%.

4. Conclusion

A series of Fe₃O₄/polyimide nanocomposites have been prepared in this research. The FT-IR characterization demonstrated the physical entanglement between the Fe₃O₄ NPs and polyimide matrix. The band gap decrease was obtained via the UV-Vis experiment. TGA and DSC test results showed that the thermal stability was improved with increasing the Fe₃O₄ NPs loading. The contact angle test indicated that more magnetic nanoparticles entangled in the PI film would increase the property of hydrophobicity of the nanocomposites. With the introduction of Fe₃O₄ NPs, dielectric property was also improved for reducing the energy loss, indicated a potential electric application in the micron electric instruments. The magnetic property has been improved and the 20% can even reach 5.21 emu.g⁻¹, indicating the potential application for magnetic area.

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