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Study of Polyarylene Ether Nitrile Terminated with Phthalonitrile/Hybrid Fe_3O_4 Nanospheres Composites by Orthogonal Experiments

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ABSTRACT: A novel series of composites of polyarylene ether nitrile terminated with phthalonitrile (PEN-*t*-Ph) filled with hybrid Fe3O4 nanospheres (h-Fe_3O_4) was prepared via *in situ* composition. Based on the cross-linking interactions between the phthalonitrile at the end of PEN-*t*-Ph molecular chains and the phthalonitrile on the surface of h-Fe_3O_4 particles to form phthalocyanine ring, it was shown that the PEN-*t*-Ph/h-Fe_3O_4 system had superior interfacial compatibility and the h-Fe_3O_4 particles were locked in the matrix resin. These results had been confirmed by scanning electron microscope analysis. By orthogonal experiments and statistic analysis, the optimal conditions of cure temperature, type of h-Fe_3O_4 and content of h-Fe_3O_4 had been determined. Meanwhile, the results of range analysis and variance analysis indicated that the cure temperature had great effects on the thermal properties. Thermal studies revealed that the glass transition temperature of PEN-*t*-Ph/h-Fe_3O_4 cured at 320°C was 214.7°C, increased by about 40°C compared to the PEN-*t*-Ph/h-Fe_3O_4 without heat treatment, and the temperature corresponding to the weight loss of 5 wt % was increased by about 20°C. Mechanical measurements indicated that PEN-*t*-Ph/h-Fe_3O_4 cured at 320°C possesses excellent mechanical properties with tensile strength of 93.33 MPa and tensile modulus of 2414.05 MPa, 9.91 MPa, 355.76 MPa higher than pure PEN-*t*-Ph film cured at 320°C, and 13.26 MPa, 397.90 MPa higher than PEN-*t*-Ph/h-Fe_3O_4 without heat treatment. Most importantly, the presence of h-Fe_3O_4 particles endows PEN-*t*-Ph/h-Fe_3O_4 system with good magnetic property. Thus, PEN-*t*-Ph/h-Fe_3O_4 cured at 320°C may have potential applications in field of magnetic materials. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40418.

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INTRODUCTION

As a well-known type of engineering thermoplastic resin, polyarylene ether nitriles (PEN) have attracted considerable attention due to their outstanding properties including excellent thermal and thermo-oxidative stability, good mechanical properties, superior chemical inertia, and radiation resistance.[1–3] Moreover, as a crosslinkable PEN, polyarylene ether nitrile terminated with phthalonitrile (PEN-*t*-Ph) has a wide range of applications owing to its more excellent thermal stability, better mechanical properties.[4] It is due to the fact that the phthalonitrile at the end of the PENs molecular chain can react between each other to form the thermally stable phthalocyanine rings.

In recent decades, polymer/inorganic composites have attracted considerable attention for their unique properties. Many types of filler materials have been used to improve the properties of the matrix resin, such as mineral fillers or glass beads to increase heat distortion temperature, carbon nanotubes to augment the thermal transport properties and fibrous fillers to improve tensile strength.[5–7] However, these excellent properties of the resulted materials depend on several factors, such as the chemical bonding of the filler and matrix at the interface and the interfacial compatibility between the dispersed phase and matrix.[8] For instance, the mechanical properties of the polymers, such as impact strength, tensile strength and impermeability to solvents and oxygen can be significantly affected by both the size and the shape of the dispersed phase in an incompatible polymer blend.[9,10] Therefore, many researchers had done great effort to solve the problem of interfacial compatibility which limit the employment of fillers to polymers. As has been reported, the interfacial compatibility between the filler and matrix can be improved via the surface functionalization of filler materials.[11,12]

Fe_3O_4 nanoparticles have received a lot of attention because of their promising magnetic properties and potential applications in color imaging, electromagnetic shielding, magnetic recording

Table I. Testing Factors and Levels

Factors		Cure temperatures (°C)	Types of h-Fe_3O_4	Contents of h-Fe_3O_4 (wt %)
Symbols		*T*	*B*	*C*
Levels	1	300	a	2
	2	320	b	4
	3	340	c	6

media and soft magnetic materials.[13] In the current study, Fe_3O_4 hybrid nanospheres (h-Fe_3O_4) were prepared from the PEN-*t*-Ph, $FeCl_3{\cdot}6H_2O$, ethyleneglycol, and polyethyleneglycol by one-step solvothermal method to solve the interfacial compatibility with the PEN-*t*-Ph matrix.[14] And a series of composites of PEN-*t*-Ph filled with h-Fe_3O_4 particles were synthetized via *in situ* composites.

Orthogonal experiments can qualitatively analyze the correlations among the relevant variables at different levels through designing orthogonal table and statistic analysis.[15] Regressive analysis can be used to get the optimized parameters, to achieve the predetermined features, and to uncover the statistic principle based on the hidden or equivocal factors.[16] The orthogonal table $L_9(3)^4$ was used in this work, and the glass transition temperature (T_g), the temperature corresponding to the weight loss of 5 wt % ($T_{5\%}$), tensile strength, tensile modulus and breaking elongation were set as the investigation targets. Three influential factors including cure temperature, type of PEN-*t*-Ph/Fe_3O_4 hybrid nanospheres (h-Fe_3O_4) and content of h-Fe_3O_4 were chosen, and three levels were set for each factor. Through the range analysis and variance analysis, the optimal cure temperature, type of h-Fe_3O_4, and content of h-Fe_3O_4 had been determined. Finally, the effect of the h-Fe_3O_4 and cure temperature on the thermal and mechanical properties of the matrix resin had been investigated; besides, the magnetic property of the PEN-*t*-Ph/h-Fe_3O_4 film also had been investigated.

EXPERIMENTAL

Materials

The PEN-*t*-Ph was synthesized in our laboratory. Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, 99%), ethyleneglycol (EG, 99%), and polyethyleneglycol 2000 (PEG, 99%) were purchased from Kelong Regent Co., Chengdu, China. Anhydrous ethanol (CH_3CH_2OH, 99%), *N*-methylpyrrolidone (NMP, purity 99%) were purchased from Tianjin Bodi Chemical Holding Co., Tianjin, China. Based on the different mass ratio between the PEN-*t*-Ph and $FeCl_3{\cdot}6H_2O$, the different types of h-Fe_3O_4 had been prepared, and the mass ratios between the PEN-*t*-Ph and $FeCl_3{\cdot}6H_2O$ of type **a**, **b**, and **c** were 1/19, 1/9, and 1/3, respectively.

Orthogonal Experimental Design

To investigate the effect of the cure temperature, type of h-Fe_3O_4 and content of h-Fe_3O_4 on the properties of PEN-*t*-Ph/h-Fe_3O_4 crosslinking films, the orthogonal experiments have been designed, and the testing factors and levels were listed in Table I. The orthogonal experiment table $L_9(3)^4$ was arranged, and the testing program was listed in Table II in detail. Finally, optimal *in situ* composite conditions and significant factors were

Table II. Testing Program and the Corresponding Results

Test numbers	Cure temperatures	Types of h-Fe_3O_4	Contents of h-Fe_3O_4	Error column	Test index
1	1 (T_1)	1 (B_1)	1 (C_1)	1	y_1
2	1 (T_1)	2 (B_2)	2 (C_2)	2	y_2
3	1 (T_1)	3 (B_3)	3 (C_3)	3	y_3
4	2 (T_2)	1 (B_1)	2 (C_2)	3	y_4
5	2 (T_2)	2 (B_2)	3 (C_3)	1	y_5
6	2 (T_2)	3 (B_3)	1 (C_1)	2	y_6
7	3 (T_3)	1 (B_1)	3 (C_3)	2	y_7
8	3 (T_3)	2 (B_2)	1 (C_1)	3	y_8
9	3 (T_3)	3 (B_3)	2 (C_2)	1	y_9
I_j	$I_1 = y_1 + y_2 + y_3$	$I_2 = y_1 + y_4 + y_7$	$I_3 = y_1 + y_6 + y_8$		
II_j	$II_1 = y_4 + y_5 + y_6$	$II_2 = y_2 + y_5 + y_8$	$II_3 = y_2 + y_4 + y_9$		
III_j	$III_1 = y_7 + y_8 + y_9$	$III_2 = y_3 + y_6 + y_9$	$III_3 = y_3 + y_5 + y_7$		
k_j	$k_1 = 3$	$k_2 = 3$	$k_3 = 3$		
I_j/k_j	I_1/k_1	I_2/k_2	I_3/k_3		
II_j/k_j	II_1/k_1	II_2/k_2	II_3/k_3		
III_j/k_j	III_1/k_1	III_2/k_2	III_3/k_3		
Range (R_j)	max{}−min{}	max{}−min{}	max{}−min{}		
Sum of deviation square (S_j)	$S_j = k_j\left(\frac{I_j}{k_j} - \overline{y}\right)^2 + k_j\left(\frac{II_j}{k_j} - \overline{y}\right)^2 + k_j\left(\frac{III_j}{k_j} - \overline{y}\right)^2$				
Variance (V_j)	$V_j = S_j/f_j$; $V_e = S_e/f_e$; Degree of freedom $f_1 = f_2 = f_3 = f_e = 2$				
The ratio of the variance (F_j)	$F_j = V_j/V_e$				

determined from the orthogonal table established by using analysis of range and variance.

Preparation of PEN-t-Ph/h-Fe_3O_4 Crosslinking Films

The PEN-*t*-Ph/h-Fe_3O_4 crosslinking films were prepared by solution casting method combined with ultrasonic dispersion technology. First, the purified PEN-*t*-Ph was added into a three-necked flask and dissolved in the medium of NMP at 200°C for 30 min with stirring to prepare the PEN-*t*-Ph solution. Meanwhile, the h-Fe_3O_4 particles were dispersed in NMP accompanying with violent ultrasonic to form a highly dispersed suspension. Secondly, the h-Fe_3O_4 particles suspension was added into PEN-*t*-Ph solution drop by drop, and the mixture was treated with ultrasonic wave and stirred for 90 min to make sure that the h-Fe_3O_4 particles were dispersed uniformly in the polymer matrix. Thirdly, the mixture was cast on a clean glass plate, and dried in an oven to evaporate off the solvent with the procedure of 80°C, 100°C, 120°C, 140°C, 160°C, 180°C, and 200°C for 1 h, respectively. Lastly, the films were cured at higher temperature (300°C, 320°C, 340°C) for 4h to obtain the PEN-*t*-Ph/h-Fe_3O_4 crosslinking films.

Characterization

The cross-sectional morphologies of the PEN-*t*-Ph/h-Fe_3O_4 composites were characterized with scanning electron microscope (JEOL JSM-5900LV) operating at 20 kV. The thermal curing behavior of the PEN-*t*-Ph/h-Fe_3O_4 system was performed on TA Instrument DSC-Q100 with a heating rate of 10°C/min from room temperature to 350°C and a nitrogen flow rate of 50 mL/min. Thermal gravimetric analysis of the PEN-*t*-Ph/h-Fe_3O_4 system was obtained with a TA Instruments TGA-Q50 at a heating rate of 20°C/min from room temperature to 700°C under nitrogen atmosphere. The mechanical properties of the PEN-*t*-Ph/h-Fe_3O_4 films were investigated by SANS CMT6104 Series Desktop Electromechanical Universal Testing Machine. Before measurement, the films were cut into samples of 10 mm × 100 mm, and then the averaged value of the five samples was gained. The magnetic property of the PEN-*t*-Ph/h-Fe_3O_4 system was characterized by vibrating sample magnetometer (VSM, Riken Denshi BHV-525).

RESULTS AND DISCUSSIONS

Crosslinking Behavior and Morphological Properties

PEN-*t*-Ph has the crosslinkable properties due to that the terminated nitrile groups can be crosslinked to form thermally stable phthalocyanine rings.[12] The h-Fe_3O_4 particles were prepared from the PEN-*t*-Ph, $FeCl_3 \cdot 6H_2O$, ethyleneglycol and polyethyleneglycol. Therefore, the particles had been penetrated by the PEN-*t*-Ph chain, and several ends of the chain had been exposed to the surfaces of the particles. When the *in situ* composite reaction occurs between the PEN-*t*-Ph and h-Fe_3O_4, the h-Fe_3O_4 particles will be locked in the matrix resin. The corresponding schematic diagram of *in situ* composite product is shown in Figure 1(a), and the crosslinked chemical structure is shown in Figure (b).

Figure 2 shows the SEM image of the PEN-*t*-Ph/h-Fe_3O_4 crosslinking films. It can be seen that the h-Fe_3O_4 particles have great compatibility with PEN-*t*-Ph. The h-Fe_3O_4 particles exist

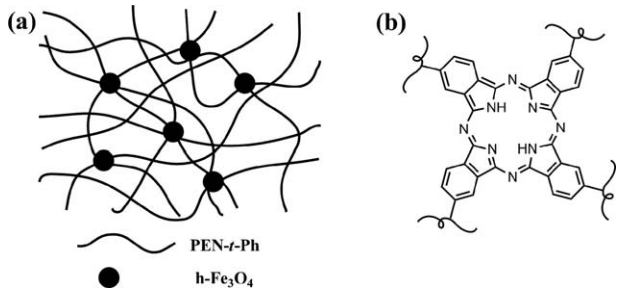

Figure 1. (**a**) Schematic diagram and (**b**) crosslinked chemical structure of *in situ* composite product.

in two kinds of forms in the resin. Some of h-Fe_3O_4 spheres have been crosslinked with the PEN-*t*-Ph and the h-Fe_3O_4 spheres are adhered to the fracture surface, which are labeled as a in Figure 2. The other h-Fe_3O_4 spheres have completely been locked in the PEN-*t*-Ph resin, which are labeled as b in Figure 2. These results are in accordance with the above theoretical analysis.

To investigate the crosslinking reaction between the PEN-*t*-Ph polymers and h-Fe_3O_4 particles qualitatively, the pure PEN-*t*-Ph and PEN-*t*-Ph/h-Fe_3O_4 films both without heat treatment are measured by DSC two times, and the DSC curves of these samples are shown in Figure 3. It is found that there is a curing peak at range 290°C–310°C in the curve of pure PEN-*t*-Ph for the first scanning, however, in the curve of pure PEN-*t*-Ph for the second scanning, this curing peak disappears. The curves of PEN-*t*-Ph/Fe_3O_4 exhibit the same phenomenon. Thus, the crosslinking reaction will take place from 290°C to 310°C both in the pure PEN-*t*-Ph and PEN-*t*-Ph/h-Fe_3O_4 films. Moreover, the T_g of PEN-*t*-Ph/h-Fe_3O_4 film for the first scanning is 171.2°C, decreased by 9.3°C than pure PEN-*t*-Ph for the first scanning with 182.9°C. It is because of that h-Fe_3O_4 is much smaller than PEN-*t*-Ph, thus the h-Fe_3O_4 particles are easy to move, and provide the space for the chain segment motion. However, the T_g of PEN-*t*-Ph/h-Fe_3O_4 film for the second

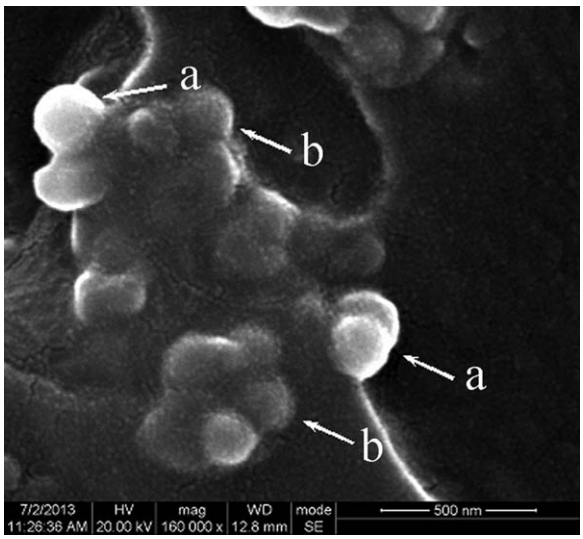

Figure 2. Cross-sectional SEM image of the PEN-*t*-Ph/h-Fe_3O_4 crosslinking films.

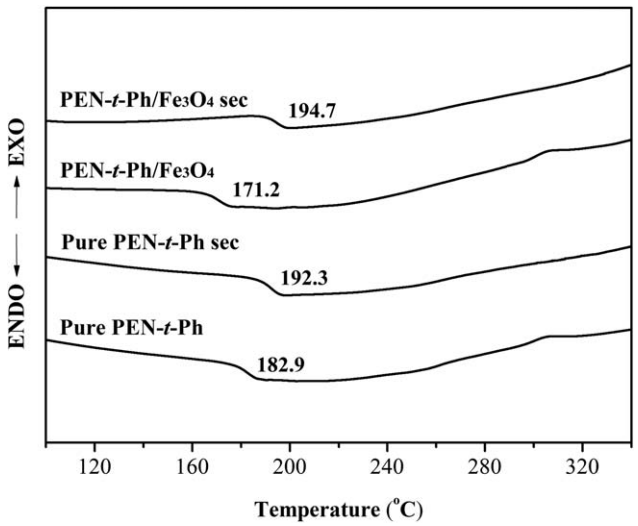

Figure 3. DSC curves of the pure PEN-*t*-Ph and PEN-*t*-Ph/h-Fe_3O_4 films.

scanning is 194.7°C, which is increased by 2.4°C than that of pure PEN-*t*-Ph for the second scanning with 192.3°C. These results indicate that loading h-Fe_3O_4 particles did not weaken the T_g of the PEN-*t*-Ph matrix after heat treatment, and h-Fe_3O_4 particles play a crosslinking agent among the crosslinking reaction of PEN-*t*-Ph.

Analysis of Orthogonal Experiment

Table III lists the thermal properties, including glass transition temperature and temperature corresponding to the weight loss of 5 wt %, and mechanical properties, such as tensile strength, tensile modulus, and breaking elongation of the PEN-*t*-Ph/h-Fe_3O_4 crosslinking films. According to the measured data and the computational formulas of range and variance analysis, the analysis results are listed in Tables IV and V.

Table IV shows the analysis results of thermal properties of PEN-*t*-Ph/h-Fe_3O_4 crosslinking films. Through the analysis of range, it can be seen that the main influencing factor of T_g is the cure temperature, followed by the type of h-Fe_3O_4, and the order of influencing factor of $T_{5\%}$ is the same as that of T_g. Thus, the main factor affecting its thermal performance is the cure temperature which should be chosen as 340°C. To the test index of T_g, it can be found that the $F_{0.01} > F_1 > F_{0.05}$ from the analysis of variance, so the condition of cure temperature has great influence on the T_g of PEN-*t*-Ph/h-Fe_3O_4 crosslinking films. And the values of F of both the type of h-Fe_3O_4 and content of h-Fe_3O_4 are below the $F_{0.1}$, so it is clear that they have no significant effect on the T_g of PEN-*t*-Ph/h-Fe_3O_4 crosslinking films. To the test index of $T_{5\%}$, all the conditions of cure temperature, type of h-Fe_3O_4 and content of h-Fe_3O_4 have no significant effect on index. In conclusion, the key factor affecting the thermal performance of PEN-*t*-Ph/h-Fe_3O_4 crosslinking films is the cure temperature. It is due to the fact that the cross-linking interactions between the cyano groups would form phthalocyanine ring which have stable structure at high temperature, so that the thermal performance of the polymer can be improved through the cure temperature increased.

Table V lists the analysis results of mechanical properties of PEN-*t*-Ph/h-Fe_3O_4 crosslinking films. From analysis of range, it is found that the order of the effect factors on the tensile strength is: type of h-Fe_3O_4 > cure temperature > content of h-Fe_3O_4. The order of the effect factors on the tensile modulus is: content of h-Fe_3O_4 > type of h-Fe_3O_4 > cure temperature, and the influence of the type of h-Fe_3O_4 and content of h-Fe_3O_4 is greater than cure temperature significantly. The order of the effect factors on the breaking elongation is: type of h-Fe_3O_4 > content of h-Fe_3O_4 > cure temperature. In conclusion, the main effect factor on the tensile strength and breaking elongation is the type of h-Fe_3O_4, and the main effect factor on tensile modulus is the content of h-Fe_3O_4. Thus, the type of h-Fe_3O_4 should be selected b, and the content of h-Fe_3O_4 should be selected 6.0 wt %. By comprehensive consideration of thermal, mechanical properties and process cost, 320°C would be the most optimal cure temperature.

From the analysis of variance, all the values of F to mechanical properties are below the value of $F_{0.1}$, so the factors of cure temperature, types of h-Fe_3O_4, and contents of h-Fe_3O_4 have no significant effect on mechanical properties. Therefore, the condition of *in situ* composite is mainly decided by the results of the range analysis.

Thermal and Mechanical Properties

To investigate the influence of the h-Fe_3O_4 and cure temperature on the thermal and mechanical properties of the matrix

Table III. Thermal and Mechanical Properties of PEN-*t*-Ph/h-Fe_3O_4 Crosslinking Films

Test numbers	T_g (°C)	$T_{5\%}$ (°C)	Tensile strength (MPa)	Tensile modulus (MPa)	Breaking elongation (MPa)
1	209.2	525.17	89.48	2332.64	7.75
2	209.0	522.51	87.81	2297.12	6.94
3	205.4	518.73	87.03	2461.41	6.06
4	225.5	522.97	86.71	2470.40	5.72
5	214.7	518.77	93.33	2414.05	8.02
6	214.5	525.95	88.08	2218.40	6.87
7	236.0	529.45	63.50	2435.06	3.43
8	228.0	522.69	91.24	2336.91	7.15
9	228.3	534.99	82.03	2167.49	5.99

Table IV. Analysis Results of Thermal Properties of PEN-*t*-Ph/h-Fe_3O_4 Crosslinking Films

Results analysis	Cure temperatures	Types of h-Fe_3O_4	Contents of h-Fe_3O_4	Error column
Glass transition temperature				
I_j/k_j	207.87	223.57	217.23	
II_j/k_j	218.23	217.23	220.93	
III_j/k_j	230.77	216.07	218.70	
R_j	22.90	7.50	3.70	
V_j	394.48	48.86	10.41	5.47
F_j	72.06	8.93	1.90	
Temperatures Corresponding to the Weight Loss of 5 wt %				
I_j/k_j	522.14	525.86	524.60	
II_j/k_j	522.56	521.32	526.82	
III_j/k_j	529.04	526.56	522.32	
R_j	7.10	5.24	4.50	
V_j	44.94	24.24	15.23	21.96
F_j	2.05	1.10	0.69	

resin, the pure PEN-*t*-Ph film cured at 320°C and PEN-*t*-Ph/h-Fe_3O_4 film without any heat treatment were prepared.

Thermally induced phase transition behavior of the PEN-*t*-Ph/h-Fe_3O_4 system was investigated by DSC under a nitrogen atmosphere. Figure 4 shows the DSC curves of the pure PEN-*t*-Ph film cured at 320°C labeled as (**1**), PEN-*t*-Ph/h-Fe_3O_4 film without heat treatment labeled as (**2**) and sample **5** of PEN-*t*-Ph/h-Fe_3O_4 film labeled as (**3**). It can be seen that the T_g of samples (**1**), (**2**), and (**3**) are 212.7°C, 171.2°C, and 214.7°C, respectively. The T_g of samples (**1**) and (**3**) which cured at 320°C for 4 h are almost the same, and increased by about 40°C compared to the T_g of sample (**2**). These results indicate that and loading h-Fe_3O_4 particles have little effect on the T_g, and the T_g increased greatly through the method of heat

Table V. Analysis Results of Mechanical Properties of PEN-*t*-Ph/h-Fe_3O_4 Crosslinking Films

Results analysis	Cure temperatures	Types of h-Fe_3O_4	Contents of h-Fe_3O_4	Error column
Tensile strength				
I_j/k_j	88.11	79.90	89.60	
II_j/k_j	89.37	90.79	85.52	
III_j/k_j	78.92	85.71	81.29	
R_j	10.45	10.89	8.31	
V_j	97.57	89.19	51.84	72.37
F_j	1.35	1.23	0.72	
Tensile modulus				
I_j/k_j	2363.72	2412.70	2295.98	
II_j/k_j	2367.62	2349.36	2311.67	
III_j/k_j	2313.15	2282.43	2436.84	
R_j	54.47	130.27	140.86	
V_j	2769.37	12,730.27	17,877.10	12,679.81
F_j	0.22	1.00	1.41	
Breaking elongation				
I_j/k_j	6.92	5.63	7.26	
II_j/k_j	6.87	7.37	6.22	
III_j/k_j	5.52	6.31	5.84	
R_j	1.40	1.74	1.42	
V_j	1.88	2.30	1.62	1.74
F_j	1.08	1.32	0.93	

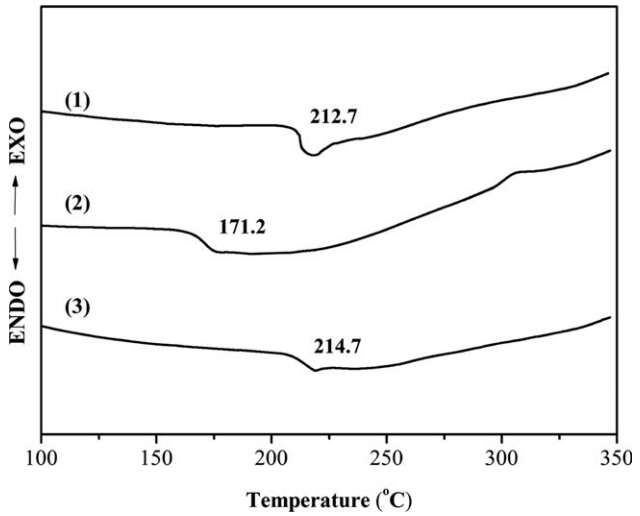

Figure 4. DSC curves of the samples: (**1**) Pure PEN-*t*-Ph film cured at 320°C; (**2**) PEN-*t*-Ph/h-Fe_3O_4 film without heat treatment; (**3**) PEN-*t*-Ph/h-Fe_3O_4 film cured at 320°C.

treatment. Therefore, the applicable temperature will be improved effectively.

From the thermogravimetric curves of the samples (**1**), (**2**), and (**3**) shown in Figure 5, it is found that the curve of sample (**1**) is similar to that of sample (**3**) before 600°C. However, the temperature corresponding to the weight loss of 5 wt % of sample (**2**) without heat treatment is below than that of samples (**1**) and (**3**) obviously. It can be seen that the $T_{5\%}$ of samples (**1**) and (**3**) increased by about 20°C than that of samples (**2**), and $T_{10\%}$ increased by about 15°C. The temperature corresponding to the maximum rate of loss mass (T_m) of the samples are much the same. These results demonstrate that the thermostability of the films was improved greatly after heat treatment, so that the using temperature of the polymers is improved.

The h-Fe_3O_4 particles have a little influence on the thermal properties of the polymer from the above analysis. However,

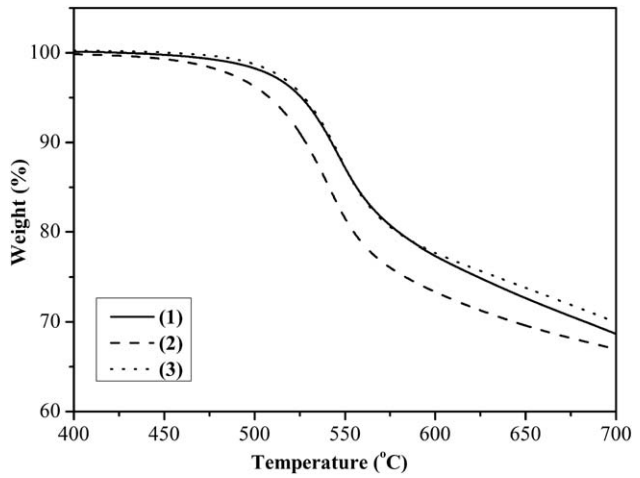

Figure 5. Thermogravimetric curves of the samples: (**1**) Pure PEN-*t*-Ph film cured at 320°C; (**2**) PEN-*t*-Ph/h-Fe_3O_4 film without heat treatment; (**3**) PEN-*t*-Ph/h-Fe_3O_4 film cured at 320°C.

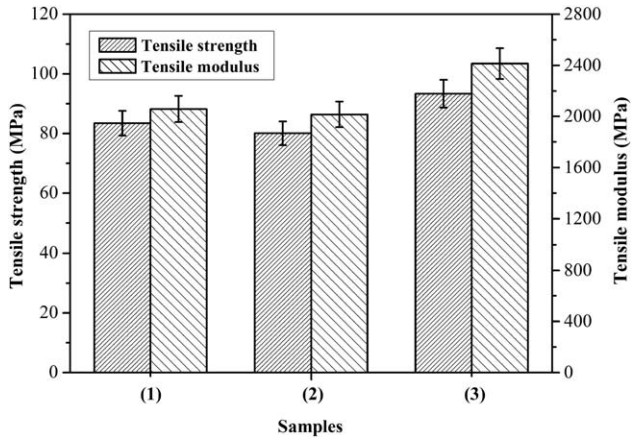

Figure 6. Mechanical properties of the samples: (**1**) Pure PEN-*t*-Ph film cured at 320°C; (**2**) PEN-*t*-Ph/h-Fe_3O_4 film without heat treatment; (**3**) PEN-*t*-Ph/h-Fe_3O_4 film cured at 320°C.

they have great effect on the mechanical properties of the composites. Figure 6 shows the mechanical properties of samples (**1**), (**2**), and (**3**). The tensile strength of samples (**1**), (**2**), and (**3**) are 83.42 MPa, 80.07 MPa, 93.33 MPa, and the tensile modulus are 2058.29 MPa, 2016.25 MPa, and 2414.05 MPa, respectively. These results indicate that loading h-Fe_3O_4 particles make the tensile strength increase by 9.91 MPa, and make the tensile modulus increase by about 355.76 MPa. Heat treatment makes the tensile strength increase by 13.26 MPa, and makes the tensile modulus increase by about 397.90 MPa. Therefore, both loading h-Fe_3O_4 particles and heat treatment can improve the mechanical properties of polymers. This reason can be explained from two aspects. On the one hand, through heat treatment, the cyano groups at the end of PEN-*t*-Ph or on the surface of h-Fe_3O_4 particles can react with each other to form phthalocyanine ring, causing the mechanical properties to improve. On the other hand, loading h-Fe_3O_4 particles reduce the relative motion of the polymer molecular chain, and prevent the propagation of the crack when the crack extension encountered h-Fe_3O_4 particles.

Magnetic Properties

The magnetic property of PEN-*t*-Ph/h-Fe_3O_4 system will be endowed by the presence of h-Fe_3O_4 particles. Figure 7 shows the magnetic hysteresis loop of the sample 5 of PEN-*t*-Ph/h-Fe_3O_4 film. The saturation magnetization (M_s) is the achieved maximum value that the magnetization intensity of ferromagnetic material and the ferromagnetic materials increases with increasing magnetic field, and this value of the PEN-*t*-Ph/h-Fe_3O_4 film is 5.18 emu g^{-1}. The remnant magnetization (M_r) is the residual magnetization after the applied field is reduced to zero, and this value of PEN-*t*-Ph/h-Fe_3O_4 film is 1.15 emu g^{-1}. The coercivity (H_c, Oe) is the external applied magnetic field necessary to return the material to a zero magnetization condition, and this value of PEN-*t*-Ph/h-Fe_3O_4 film is 168.13 Oe at 300 K. These results indicate that the PEN-t-Ph/h-Fe_3O_4 system possesses superior magnetic property, and the potential applications of PEN-*t*-Ph/h-Fe_3O_4 film in the magnetic field are fantastic.

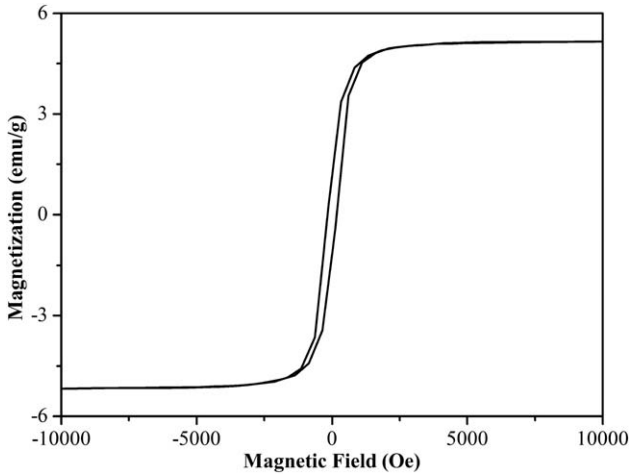

Figure 7. Magnetic hysteresis loop of typical PEN-*t*-Ph/h-Fe_3O_4 film.

CONCLUSIONS

A novel series of PEN-*t*-Ph/h-Fe_3O_4 *in situ* composites were successfully prepared, and this system possessed excellent interfacial compatibility between fillers and matrix, which had been confirmed by the analysis of scanning electron microscope image. It was because of the cross-linking interactions between the PEN-*t*-Ph molecular chains and the h-Fe_3O_4 particles that phthalocyanine ring will be formed at high temperature. Through orthogonal experimental design and statistic analysis, the optimal conditions of cure temperature, type of h-Fe_3O_4 and content of h-Fe_3O_4 had been determined. Meanwhile, the results of range analysis and variance analysis indicated that the cure temperature had great effect on the thermal properties. Thermal studies revealed that the glass transition temperature of PEN-*t*-Ph/h-Fe_3O_4 cured at 320°C was 214.7°C, increased by about 40°C compared to the PEN-*t*-Ph/h-Fe_3O_4 without heat treatment, and the temperature corresponding to the weight loss of 5 wt % increased by about 20°C. Mechanical measurement indicated that both the method of loading h-Fe_3O_4 particles and heat treatment could improve the mechanical properties of polymers, and PEN-*t*-Ph/h-Fe_3O_4 cured at 320°C possessed excellent mechanical properties with tensile strength of 93.33 MPa and tensile modulus of 2414.05 MPa. Besides, the presence of h-Fe_3O_4 particles endows PEN-*t*-Ph/h-Fe_3O_4 system with good magnetic property. Therefore, the system of PEN-*t*-Ph/h-Fe_3O_4 cured at 320°C will be a candidate to be applied in high temperature conditions.

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