

## Effect of $K_{0.5}Na_{0.5}NbO_3$ Filling Particles on the Charge Carrier Trap Distribution of Polyimide Films

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**ABSTRACT:** Polyimide (PI) films filled with  $K_{0.5}Na_{0.5}NbO_3$  (KNN50) particles at different weight 0, 5, 10, and 15 wt % had been prepared by in-situ dispersion polymerization process. The thermally stimulated current (TSDC) method was used to investigate the charge carrier trap levels and their distribution of the composite films. The TSDC spectra show that pure film has  $\alpha$ -peaks and  $\beta$ -peak, but the composite films only have  $\alpha$ -peaks and an extraordinary peak at high temperature region. The trap parameters were calculated by an approximate model, and the results indicate that charge released of the shallow traps show a nonlinear behavior. The trap energies decrease from 0.879–0.968 eV to 0.549–0.839 eV with the increase of the KNN50 content. The surface and interface between KNN50 and PI matrix was considered to the variation of the trap levels. The extraordinary peak of the composite films was correlated with the phase transition of the KNN50 particles. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39828.

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### INTRODUCTION

Dielectric polymer films have been widely used for insulating materials and electret materials due their excellent physical, chemical and charge storage properties. The failure of the insulating materials often occurs in the pulse and serious electrostatic hazards, which are caused by electrostatic discharge due to charged dielectrics.<sup>1,2</sup> Research on polymer composite had recently attracted interest for its multiple functions as electric devices.<sup>3–5</sup> On the one hand, the composite could obtain remarkable properties, but on the other hand, the filler particles would affect the charge carrier trap in the films.<sup>6</sup> For the dielectric materials, its electrical properties are closely related to the charge carrier trap. It has been considered that charge carrier traps in a substance play an important role in the charging phenomenon.<sup>7</sup> Therefore, choosing suitable filler particles and finding the optimal concentration of the addition particle become the key point.

Ferroelectric-ceramic/polymer composite materials have been considered as the most promising materials for dielectric materials. Because they can combine the excellent dielectric characteristics of ceramic material and the good mechanical strength and easy process ability of polymer material, thus having the capability to improve the electrical performance as well as to reduce the size and cost of electronic systems.<sup>8–11</sup> PI is one of the major dielectrics for industrial applications. It has been

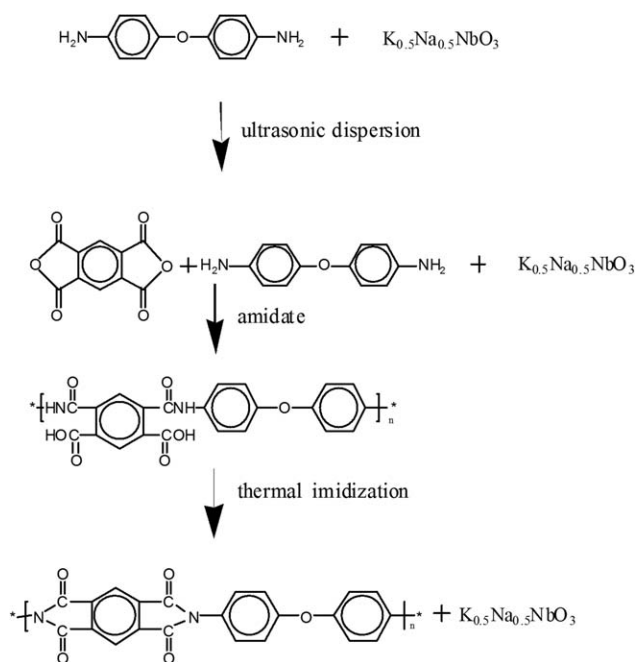
widely used as an electret material and electrical insulator. The trap and charge transport of PI films have been intensively studied.<sup>2,9</sup> Additionally, the materials based on potassium-sodium niobate solid solution  $K_{1-x}Na_xNbO_3$  have recently become a focus of interest as an alternative system for lead containing functional material. It was found that the  $K_{0.5}Na_{0.5}NbO_3$  (KNN50) exhibits optimum piezoelectric response. However, the KNN50 particles-filled PI material and the charge carrier trap of the composite have not been reported.

In this paper, the effect of KNN50 particle on the charge carrier trap of the PI was studied. As a most effective and commonly method, thermally stimulated current has provided an effective tool to study charge carrier traps in materials. The TSDC characterizations of PI composite films incorporate with KNN50 contents of 0, 5, 10, 15 wt % were represented. The evaluated charge carrier trap parameters from TSC spectra of KNN50-filled PI film were also calculated. The relationships between the variations of the charge carrier trap distribution, the charge released quantity and the surface and interface introduced by KNN50 were analyzed.

### EXPERIMENTAL

#### Preparation of Experimental Sample

KNN50 powder was prepared by conventional ceramic sintering technique. High-purity (99.99%) Potassium carbonate ( $K_2CO_3$ ),



**Figure 1.** Preparation of KNN50 particles-filled PI films.

sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and niobium oxide (Nb<sub>2</sub>O<sub>5</sub>) were used as raw materials. They were milled in polytetrafluoroethylene with agate balls for 24 h using ethanol as a medium. After calcination at 800°C for 4 h, the calcined powder was ball milled again for 48 h. Finally, the particles were dried as the filler particle. The pure PI films and composite films were both prepared using *in-situ* dispersion polymerization process with pyromellitic dianhydride (PMDA), 4,4'-diaminodiphenyl ether (ODA) and KNN50 particles. The composite films preparation process was shown in Figure 1. The ODA and DMAC were added into a three-necked flask with a stirrer. After complete dissolution of ODA in DMAC, a precalculated amount of KNN50 filler was added into the solution and then ultrasonic was applied to the mixture for 20–40 min to yield a suspension with KNN particles homogeneously dispersed. PMDA was

added into the suspension in six portions to ensure the complete dissolution of the previous portion. Each portion was added at intervals of 6 min. When PMDA was completely added and dissolved, the suspension was vigorously stirred for a further 2 h at room temperature to yield a sticky and homogeneous mixture of PAA and KNN particles in DMAC. The films with the KNN50 content of 0, 5, 10, and 15 wt % were made by coating the PAA or PAA/KNN50 solutions onto a clean glass plate by an automatic film applicator. Here, the thermal imidization was performed through a seven-step cure process (80°C/40 min, 150°C/30 min, 175°C/30 min, 195°C/30 min, 235°C/30 min, 275°C/30 min, 320°C/30 min) under an air atmosphere. The composite films preparation process is shown in Figure 1. On cooling process, the films were stripped off the glass surface by immersion of the glass plate into pure water. The average thickness of the films is 20–25 μm in final.

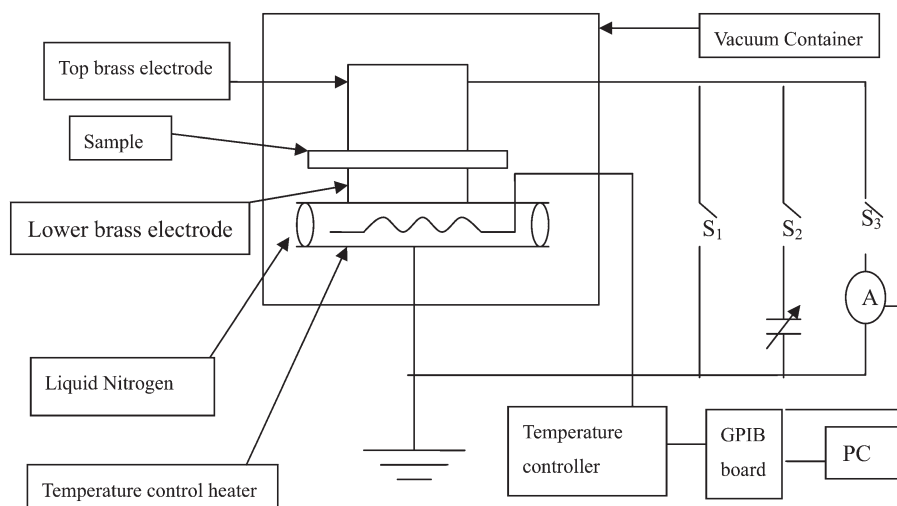
The structures of the films were studied using a Fourier Transform Infrared spectroscopy (FTIR, Avatar 370, Thermo Nicolet Corporation, America). The microstructures were studied by scanning electron microscopy (SEM, Quanta 200, FEI Sieioa, Netherlands).

#### TSDC Testing

**Samples Preparation.** The specimens of test were the pure PI and composite films with KNN50 content of 5, 10, and 15 wt %. The films were cut into 60 × 60 mm<sup>2</sup> specimens, and gold electrodes with 40 mm diameter were sputter-coated on the both sides. In order to remove residual charges, the specimens were placed in a thermostatic oven at 160°C and dried for 24 h.

**TSDC Experimental Procedure.** Figure 2 shows the circuit used for the TSDC measurements. DC is a dc voltage source (DW N153-5AC, Tianjin, China) used for poled the sample. Liquid nitrogen is used for cooling and a stabilized power supply is used for heating the sample. The detail is as follows.

1. The sample was electrically shorted at room temperature by closing switch S1 and opening switches S2 and S3. Then it



**Figure 2.** Schematic illustration of TSDC experimental measurement.

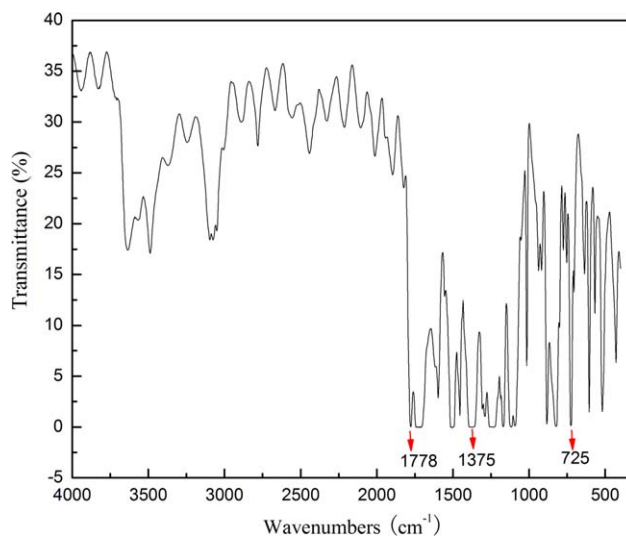
was poled at 453 K ( $T_b$ ) and  $-50$  KV/mm ( $E_b$ ) for 30 min, by opening S1, S3, and closing S2.

- The sample with space charge, which was formed at the polarization conditions, was cooled down rapidly by liquid  $N_2$  from  $T_b$  to 213 K by closing S2. Then it was shorted instantly by opening S2 and closing S1. Subsequently, S1 was opened and S3 was closed.
- After removing the DC biasing stress, the TSDC spectra were measured by closing S3 using an electrometer (6517A, Keithley, USA).

## RESULT AND DISCUSSION

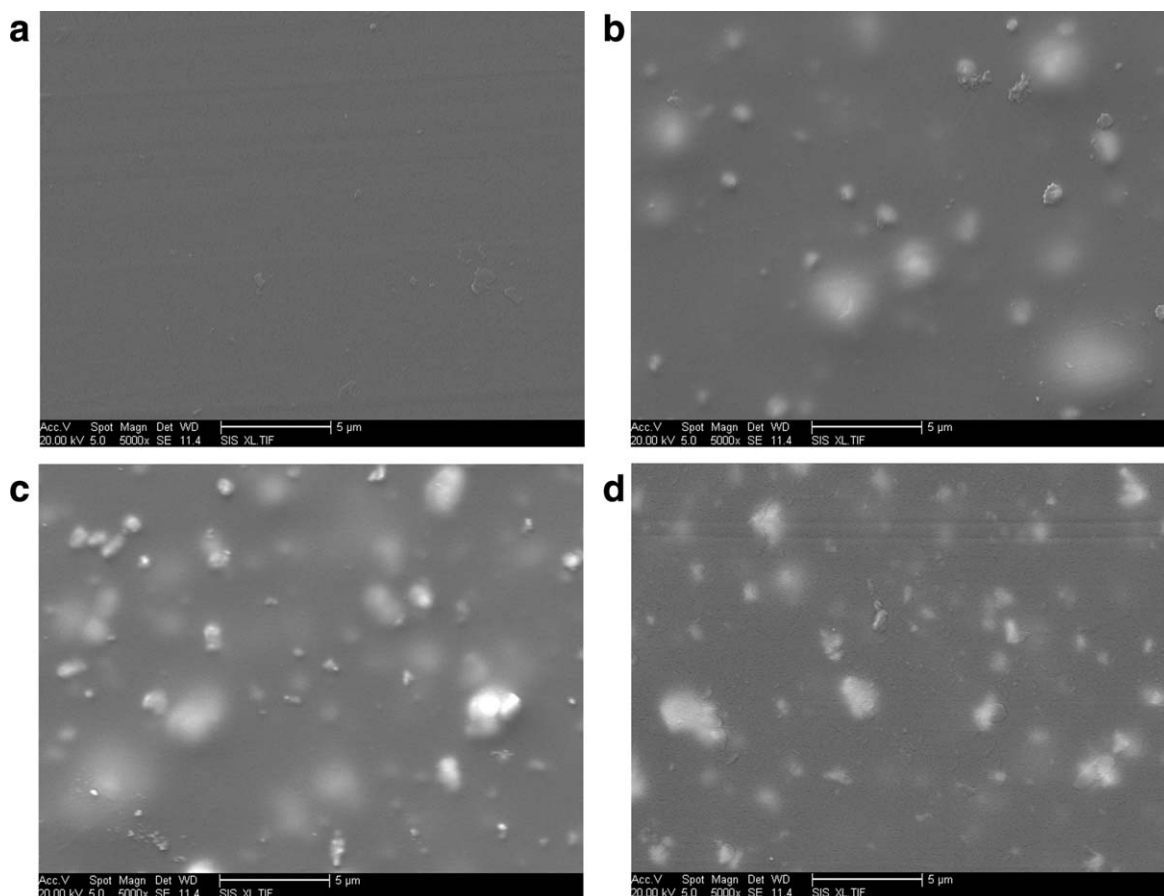
The chemical structures of the films were studied by FTIR spectroscopy. The FTIR spectrum of pure PI films, as shown in Figure 3, shows that the characteristic imide groups are observed. The peaks near  $725\text{ cm}^{-1}$  denote the C=O bending, the peaks at about  $1375\text{ cm}^{-1}$  represent C—N stretching, and that of  $1778\text{ cm}^{-1}$  indicate C=O asymmetric stretching, which confirmed polyimide formation. And the structure characterization of KNN50 has been introduced in our previous presented papers.<sup>12</sup>

Figure 4 shows surface morphology of KNN50-filled PI films, which is obtained by scanning electron microscopy (SEM). As shown in Figure 4(a), the pure PI film is smooth and clean. With the KNN50 ceramic grains added, it can be observed that



**Figure 3.** FTIR spectrum of pure PI films. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

KNN50 filler is well dispersed in PI matrix, as shown in Figure 4(b–d). And the size of KNN50 ranges from about  $0.5$  to  $3\text{ }\mu\text{m}$ . The surface morphological image of the hybrid film with 15 wt % KNN50 filler is shown in Figure 4(d). It can be seen that, even with 15 wt % KNN50 loading, KNN50 filler still can be



**Figure 4.** SEM morphology of a fresh surface of the pure and KNN particles-filled PI films (a) 0 wt %, (b) 5 wt %, (c) 10 wt %, and (d) 15 wt %.

well dispersed in the PI matrix without any badly accumulation, which can be attributed to the in situ polymerization. It confirms that the KNN50 fillers are homogeneously dispersed into the PI matrix.

The TSDC spectra of pure PI and 5, 10, 15 wt % composite samples were shown in Figure 5. Because of the high measuring frequency, there is some burr in the curve. In this paper, the adjacent-averaging method was used to smoothing the original curves. It can be seen from the figure that the pure PI has two kinds of peaks, which are characterized as  $\beta$ - and  $\alpha$ -peaks, in the increasing order of temperature. The  $\beta$ -peaks are associated with dipolar orientation relaxation process; whereas  $\alpha$ -peaks are associated with space charge polarization, which seem to be initiated by the macromolecular relaxation or more precisely the relaxation in the crystalline regions.<sup>2</sup> With the addition of KNN50 particles, the  $\beta$ -peaks disappear. In other words, the composite films only have  $\alpha$ -peaks. The same results had been reported in the inorganic/polymer composite, such as PA/BaTiO<sub>3</sub> and SiO<sub>2</sub>/PI composite film.<sup>3,4</sup>

It can be seen from the figure that the TSDC curves have multi peak shape. Therefore, the classical single-peak analysis method is no longer suitable for precise determination of the trap signatures due to the mutual interferences between overlapping peaks over a wide range. To studies the trap levels of the films, the Gaussian fitting were used to the multi curves detaching, as shown in

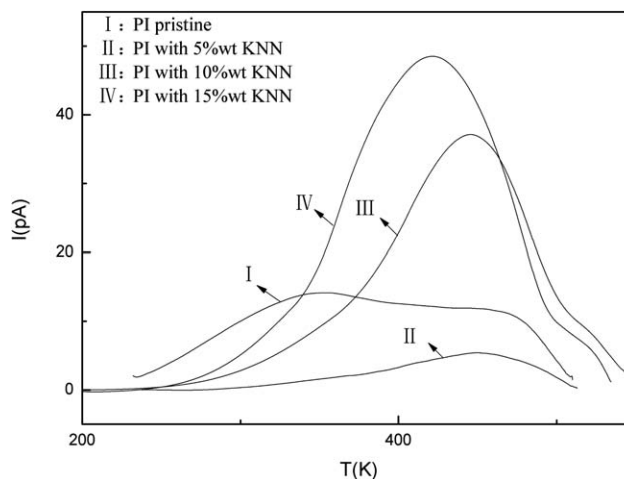


Figure 5. TSDC curves of the pure and KNN50 particles-filled PI films.

Figure 6. The origin curves, detached curves by Gaussian fitting and the sum of the detached line were denoted by  $a_{\infty}$ ,  $b_{\infty}$ ,  $c_{\infty}$  respectively. All the coefficients of determination (COD)  $R^2$  of fitting are better than 99.9%, as inset in the figures, which indicate the better correlation between the fitting and origin curves.

It has been proposed that the location of a TSDC peak can be related to the thermal activation energy for that relaxation

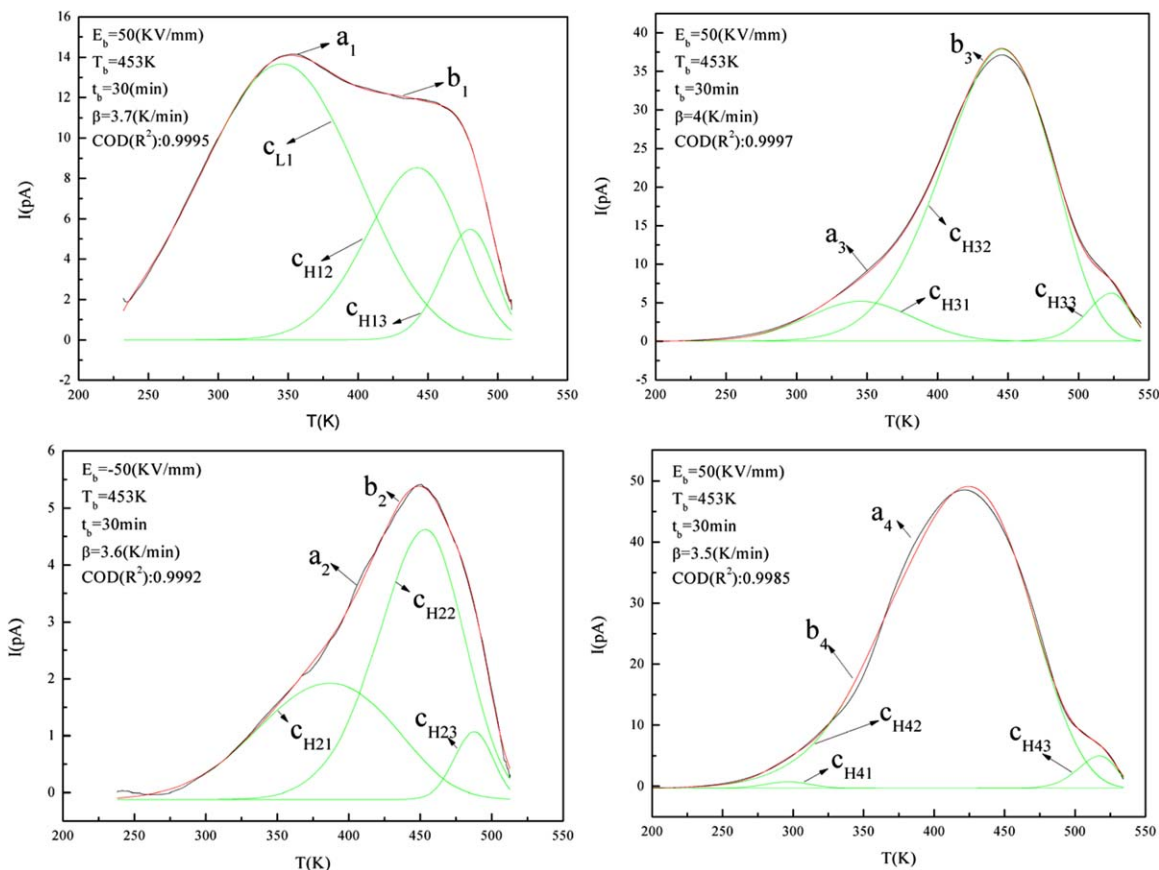


Figure 6. Fitting TSDC curves of the pure and KNN particles-filled PI films (1) 0 wt %, (2) 5 wt %, (3) 10 wt %, and (4) 15 wt %. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table I.** TSDC Parameters of Pure and KNN50 Particles-Filled PI Films

Samples	Peak	$T_p$ (K)	$I_p$ (pA)	$E_t$ (eV)	Charge released		$\tau_0$ (s)
					$Q$ ( $\times 10^{-12}$ C)		
PI	$C_{L1}$	345.3	13.66731	$0.657 \pm 0.002$	1825.660		$6.60 \times 10^{-8}$
	$C_{H11}$	442.3	8.53289	$0.879 \pm 0.002$	712.56	963.912	$3.00 \times 10^{-8}$
	$C_{H12}$	480.3	5.47523	$0.968 \pm 0.003$	251.35		$2.31 \times 10^{-8}$
5 wt % KNN50	$C_{H21}$	386.7	1.9222	$0.751 \pm 0.002$	208.35	533.672	$4.62 \times 10^{-8}$
	$C_{H22}$	453.5	4.62099	$0.906 \pm 0.002$	325.32		$2.79 \times 10^{-8}$
	$C_{H23}$	487.8	1.06232	$0.987 \pm 0.003$	5.64		$2.21 \times 10^{-8}$
10 wt % KNN50	$C_{H31}$	345.1	5.18632	$0.654 \pm 0.002$	488.39	4161.503	$6.61 \times 10^{-8}$
	$C_{H32}$	445.6	37.88819	$0.884 \pm 0.002$	3673.11		$2.93 \times 10^{-8}$
	$C_{H33}$	523.2	6.23262	$1.066 \pm 0.003$	240.92		$1.76 \times 10^{-8}$
15 wt % KNN50	$C_{H41}$	296.3	0.69654	$0.549 \pm 0.001$	40.448	6032.588	$1.07 \times 10^{-7}$
	$C_{H42}$	424.4	49.09037	$0.839 \pm 0.002$	5992.14		$3.42 \times 10^{-8}$
	$C_{H43}$	517.3	4.95776	$1.058 \pm 0.003$	250.882		$1.83 \times 10^{-8}$

process.<sup>13–15</sup> In addition, in the TSDC spectra, thermal relaxation of carrier can be correlated approximately with the relaxation temperature, as described in the study of Fang et al.<sup>16</sup> and Yu et al.<sup>17</sup>

$$E_t = kT \ln \left( \frac{T^4}{\beta} \right) \quad (1)$$

where  $k$  is the Boltzmann's constant, and  $\beta$  is the heating rate. In the measuring process, the same heating conditions of the PID controller were used using all the experiments. The heating rate  $\beta$  (divide the temperatures K/min by the heating time), which used to calculate parameters, was the obtained from the actual heating process. Small differences would be brought out during the same experiment processes. The parameter  $\beta$  obtained from the actual experiments are 3.7 K/min, 3.6 K/min, 4.0 K/min and 3.5 K/min, and the differences are consistent with the presented papers.<sup>18</sup>

If the relaxation process obeys an Arrhenius type of relationship, then

$$\tau(T) = \tau_0 \cdot \exp \left( \frac{E_t}{kT} \right) \quad (2)$$

where  $E_t$  is the energy depth of carrier trap. The pre-exponential factor  $\tau_0$  has the form

$$\tau_0 = \frac{kT_m^2}{\beta E_t} \cdot \exp \left( \frac{-E_t}{kT_m} \right) \quad (3)$$

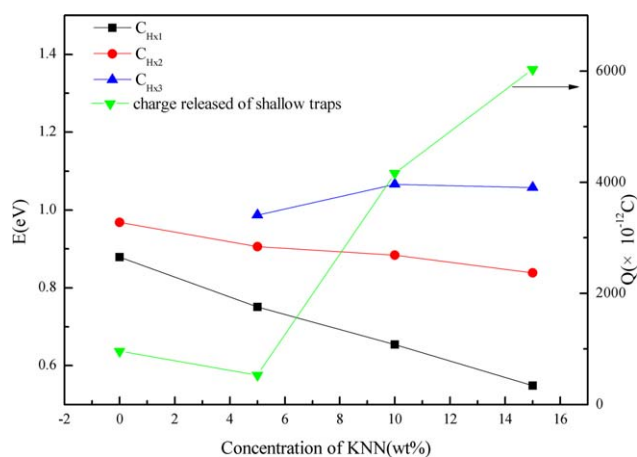
where  $T_m$  is the temperature corresponding to the maximum current. The charge released  $Q$  which can characterize the trap concentration is given by

$$Q = \int J(t) dt \quad (4)$$

The energy depth, pre-exponential factor and the charge released of the separated peaks could be obtained through the eqs. (1), (3), and (4), as shown in Table I. And in order to

study the variation of trap levels parameters clearly, the Energy and released charges of the pure and KNN50 particles-filled PI films were included in Figure 7.

It can be seen from the table and Figure 7 that only the pure films has the  $\beta$ -peak  $C_{L1}$ , and the energies ( $E_t$ ), charge released  $Q$  and pre-exponential factor  $\tau_0$  are  $0.657 \pm 0.002$  eV,  $1825.660 \times 10^{-12}$  C and  $6.60 \times 10^{-8}$  s, respectively. The energies ( $E_t$ ) of the peaks  $C_{Hx1}$  are  $0.879 \pm 0.002$  eV,  $0.751 \pm 0.002$  eV,  $0.654 \pm 0.002$  eV,  $0.549 \pm 0.001$  eV, and that of the peaks  $C_{Hx2}$  are  $0.968 \pm 0.003$  eV,  $0.906 \pm 0.003$  eV,  $0.884 \pm 0.002$  eV,  $0.839 \pm 0.002$  eV with the content of KNN50 particles 0, 5, 10, and 15 wt %, respectively. The energies ( $E_t$ ) of the two peaks Obviously decrease with the increasing content of KNN50 particles. The sum of released charges ( $C_{Hx1}$  and  $C_{Hx2}$ ) shows a nonlinear behavior. The released charge of the 5 wt % KNN50 / PI composite films is  $533.67 \times 10^{-12}$  C, which is smaller than  $963.91 \times 10^{-12}$  C of pure PI. However, it significant increases in 10 wt % and 15 wt % KNN50 composite samples,



**Figure 7.** Energy and released charges variation of the pure and KNN50 particles-filled PI films. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$4161.4 \times 10^{-12}$  C and  $6032.588 \times 10^{-12}$  C respectively. An extraordinary peak appears in the TSDC spectrum of the KNN50 composite films comparing with the pure ones. The energy of detaching peaks  $C_{Hx3}$  are  $0.987 \pm 0.003$  eV,  $1.066 \pm 0.003$  eV, and  $1.058 \pm 0.003$  eV with 5, 10, and 15 wt % KNN50 added.

It has been proposed that the peaks in TSDC spectrum are directly correlated with the associated trap concentration. It can be seen from the results noteworthy that the addition of KNN50 particles has changed the traps levels. The changed of trap parameters in composite films are correlated with the physical conformation defects and chemical defects introduced by filled particles.<sup>19–21</sup> The disappearance of the  $\beta$ -peak  $C_L$ , which indicating the shallow traps, was considered to associate with dipolar orientation relaxation. In general, amorphous polyamides exhibit the so called  $\beta$ -peak or secondary relaxation in this temperature, about 345 K, range below the glass transition.<sup>2,22</sup> At this temperature, the mobility of the macromolecular chains are very difficult, only the polarity groups mobility, such as C=O double bond, contribute to the relaxation.<sup>21</sup> The structure variation caused by the introduction of crystal KNN50 grains might take for the changes of the peak. Because the KNN50 is the ferroelectric grains, the interaction of the polarity dipolar groups and grains inhibited the mobility of these groups, which changes the trap level of the composite films.

As can be seen from Figures that the  $\alpha$ -peaks appear at about 450 K, which near the calorimetric glass transition temperature. The multi detaching peaks of the  $\alpha$ -peaks indicate the charge carries are trapped at trapping levels of at least more than one different depths. From the energies variation of the trap levels, it can be inferred that the variation of the trap levels in the composite films is caused by the physical conformation defects and chemical defects and these defects, which are introduced by the KNN50 particles addition. The  $C_{Hx1}$  and  $C_{Hx2}$  of  $\alpha$ -peaks are associated with space charge polarization, which seem to be initiated by the macromolecular relaxation or more precisely the relaxation in the crystalline regions.<sup>2</sup> It is worthy to point out that the energies of peak  $C_{Hx1}$  and  $C_{Hx2}$  decreased with the increasing of KNN50, but the charge released enhance the charge storage capacity of PI when the content of KNN50 exceed 5 wt %. It is considered that the mobility of the macromolecular chains becomes more and more difficult, but the interface between the KNN50 grains and the PI matrix increased with the increase of the fillers. The  $C_{Hx3}$  peaks, the deep trap, with the peak temperature 487.8 K, 523.2 K, and 517.3 K show that the KNN50 loading add deep trap in the PI matrix, which were considered to be caused by the phase transition of the KNN50 particles. Because the tetragonal–orthorhombic phase transition temperature of KNN50 is around 500 K.<sup>23,24</sup>

## CONCLUSIONS

This article reported the detailed investigation of the charge carrier trap in PI composite films with the KNN50 content of 0, 5, 10, and 15 wt %, by TSDC method. The introduction of KNN50 particles was effective on the charge carrier traps, distribution and their transport characteristic of the composite films. The TSDC spectra of polyamide with KNN50 composite films

were detached by Gaussian fitting, and the trap parameters were calculated from the approximate equations. The results show that the carrier trap parameters are significantly affected by filling of KNN50 particle in PI matrix. The  $\beta$ -peak disappears after addition; this type variation of the trap level was considered to be related with the mobility of the polarity dipolar groups and the interaction between that and doping grains of the composite films. It is found that the addition of KNN50 filler caused the decrease of the energy depth of carrier traps  $E_t$  from 0.879–0.968 eV to 0.549–0.839 eV, but the charge released enhances the charge storage capacity of PI when the content of KNN50 exceed 5 wt %. The decreasing mobility of the macromolecular chains, and increasing interfaces formed between the KNN50 grains and the PI matrix might responsible for the variations. Finally, the extraordinary peak of the composite films was caused by the phase transition of the KNN50 particles.

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