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A phenomenological and quantitative model for shape/temperature memory effect in polypyrrole undergoing relaxation transition

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Abstract

Purpose – To present a phenomenological and quantitative model to study the constitutive relations and working mechanism for shape/temperature memory effect in polypyrrole (PPy)-based shape memory polymers (SMPs).

Design/methodology/approach – In this paper, the origin of relaxation law was employed to theoretically predict the relationships between relaxation time and internal energy and temperature based on the thermodynamics of polymers.

Findings – A phenomenological model was proposed to quantitatively identify the factors that influence the stored mechanical energy, shape memory effect (SME) and temperature memory effect (TME) in PPy. Both structural relaxation law and Tool-Narayanaswamy (TN) model were employed to couple the constitutive relations of stress and transition temperature as a function of relaxation frequency, respectively. Furthermore, the simulation of the phenomenological model was compared with experimental results reported in relevant literature for purpose of verification.

Research implications – Exploration of the working mechanism underpinning the experimental (or phenomenal) results and significant enhancement of the understanding of relevant experimental features reported previously.

Originality/value – The outcome of this study will provide a powerful phenomenological and quantitative tool for studies on SME and TME in SMPs.

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Keywords – Shape memory polymer, Temperature memory effect, Phenomenological model, Relaxation transition

Paper type Research paper

Introduction

Stimuli-responsive polymers are one of the many types of smart materials that show noticeable changes in their properties continuously with the environmental conditions (Galaev and Mattiasson, 2010). These responsive polymers can adapt to surrounding environments in a number of ways including altering colour or transparency, changing shape (shape memory polymers, SMPs), regulating transport of ions and molecules, or converting chemical and biochemical signals into optical, electrical, thermal and mechanical signals, and vice versa (Lendlein and Kelch 2005; Crenshaw *et al.*, 2007; Cabane *et al.*, 2012; Hu *et al.*, 2012; Hoffman, 2013). As result of intensive research dedicated to this area, there are now a significant number of emerging applications of stimuli-responsive polymers being explored. Such applications include, for instance, drug delivery, diagnostics, tissue engineering and optical systems, as well as biosensors, microelectromechanical systems, coatings and textiles (Galaev and Mattiasson, 2010).

Polypyrrole (PPy) is an electrical conducting organic polymer that can be obtained by polymerisation of pyrrole (Vernitskaya and Efimov, 1997). PPy is known to have many desirable properties that allow it to be used in electronic devices (Janata and Josowicz, 2003), chemical sensors (Smela, 2003; Baughman, 2005), drug delivery, and container for proteins (Geetha *et al.*, 2006) etc. The combination of PPy with other materials to fabricate composites that combine the properties of both materials is a promising approach to extend the range of application (Baughman, 2005; Geetha *et al.*, 2006). PPy, together with other conjugated polymers, such as poly(ethylenedioxythiophene) and polyaniline etc. have been extensively studied as materials to function as artificial muscles, a technology that may offer numerous advantages over traditional motor actuating elements (Geetha *et al.*, 2006). It was found that PPy had a capability of responding to water and changing its shape, which allowed it to be classified as an SMP. Furthermore, it had been demonstrated that PPy could be used to drive motion in a rotary actuator (Okuzaki *et al.*, 1998). However, the PPy rotary actuators only output low mechanical force or power (Smela, 2003; Baughman, 2005; Geetha *et al.*, 2006; Okuzaki *et al.*, 1998). Consequently, a dynamic polymer composite was made from the rigid PPy and a flexible, interpenetrating polyolborate network (Shibayama *et al.*, 1988), which formed within the PPy matrix acting as a macromolecular counterion for PPy (Ma *et al.*, 2013). Intermolecular hydrogen bonding between the polyolborate network and PPy has been shown to alter the mechanical properties of the composite film that exchanges water with the environment to induce expansion and contraction (Ma *et al.*, 2013). Same as traditional SMPs (Tobushi *et al.*, 2001; Nguyen *et al.*, 2008; Lendlein and Kelch, 2002; Xie, 2010), PPy-based composite film also shows shape memory effect (SME) in response to water gradients. It has been demonstrated that the temperature memorisation is induced at the temperature of their initial deformation, a phenomenon known as the temperature memory effect (TME) in SMPs (Miaudet *et al.*, 2007; Sun and Huang, 2010). However, almost all previous reports are limited to experimental studies. Theoretical mechanism is a challenging problem but will significantly enhance our understanding of these experimental features. In the study that is reported in this paper, a phenomenological and quantitative model to study the constitutive relations and working mechanism for shape/temperature memory effect in PPy was established. Thus, based on relaxation law, a phenomenological model was proposed to quantitatively identify the factors that influence the stored mechanical energy, SME and TME in PPy. Both structural relaxation law and Tool-Narayanaswamy (TN) model were implemented to couple the constitutive relations of stress and transition temperature as a function of relaxation frequency, respectively. Furthermore, the simulation of the phenomenological model was compared with the available experimental results in the literature for further verification. The study aimed to provide a power phenomenological and quantitative tool for studies of SME and TME in SMPs.

An explicit form of the relaxation law

It is well understood that the thermodynamics of polymers obey the relaxation rule (Tobushi *et al.*, 2001; Nguyen *et al.*, 2008), which could be employed to theoretically predict the relationships between relaxation time and internal energy and temperature (Equation 1).

$$\tau = \tau_0 \exp\left(\Delta E_a / RT\right) \qquad (1)$$

where $\boldsymbol{\tau}$ is the relaxation time that is defined as the recovery time for SMPs in this study; $\triangle \boldsymbol{E}_\mathbf{a}$ is the activation energy of the chain mobility; R is the gas constant; and $\boldsymbol{\tau}_\mathbf{0}$ is a given constant. Both $\triangle \boldsymbol{E}_\mathbf{a}$ and $\boldsymbol{\tau}$ can be experimentally determined. Equation 1 shows that the relaxation time can be shortened by decreasing the activation energy or increasing the temperature that is the working mechanism in thermally responsive SME in SMPs. Therefore, in determining the relaxation time of an SMP, the decrease in activation energy is 'equivalent' to the increase in temperature. The relaxation time τ can be related to the frequency f via the condition $2\pi f\tau=1$, which leads to

$$\tau = 1/2\pi f \, . \tag{2}$$

Combining Equations 1 and 2, the relaxation law expressed in frequency f can be obtained (Equation 3).

$$f_{\mathrm{o}}/f = \exp\left(\Delta E_{\mathrm{a}}/RT\right) \tag{3}$$

It is necessary to qualitatively separate the effect of stored mechanical energy from the relaxation theory and Eyring equation on the activation energy ($\triangle E_{\mathrm{a}}$) of SMPs. The understanding of the origin of the shape memory effect of SMPs has been of interest to research community over the last couple of decades. Lendlein and his colleagues (Lendlein and Kelch, 2002) stated that, "These so-called plastic domains act as reinforcing filler. Their ability to deflect mechanical energy by deformation enables the growth of microcracks to be prevented". The same view was echoed by Xie (2010), "In recovery, the stored mechanical energy is released and the shape of the SMP is recovered". Therefore, it is most likely that the release of stored mechanical energy is the driving force for the memory effect in SMPs. And the memory, or recovery, quality comes from the stored mechanical energy attained during the reconfiguration and cooling of the material. Here, the activation energy ($\triangle E_{\mathrm{a}}$) equals to the stored mechanical energy in SMPs.

Constitutive modelling and stimulation

Correlation between frequency and stress undergoing relaxation transition

According to the theory on the effect of atmospheric pressure and constraint stress on the relaxation behaviour of polymers (Casalini and Roland, 2004; Bässler, 1987; Haward, 1972; He *et al.*, 1999), the relaxation law can be modified to,

$$f_{\mathrm{o}}/f = \exp\left[\left(\Delta E_{\mathrm{a}} - a\sigma\right)/RT\right] \tag{4}$$

where a is a given material constant and σ is the constraint stress applied on the polymer. Assuming that the polymer is constrained by an atmospheric pressure (P) and V is the volume change, and as $a\sigma=PV$, Equation 4 can be rewritten as,

$$f_{\mathrm{o}}/f = \exp\left[\left(\Delta E_{\mathrm{a}} - PV\right)/RT\right] \tag{5}$$

The applicability of this equation can be verified by whether the equation still balances when the atmospheric pressure (***P***) changes up and down and whether the increase in ***P*** causes a decrease in the left-hand-side of the equation (***f_o/f***), therefore increasing the flipping frequency (***f***) while the activation energy ($\triangle E_a$) and temperature (***T***) are kept constant. Based on Equation 5, it can be seen that the frequency gradually increases with an increase in saturated water vapour pressure as shown in a previous report (Ma *et al.*, 2013). Figures 1 plots numerical results for output power as a function of frequency at a variety of temperatures. The numerical results reveal the trend as expected, i.e. with an increase in the frequency of shape change in SMPs, the output power (in the form of output stress strength) in the shape recovery is gradually increased. Furthermore, the effect of temperature on the output power can also be seen. Thus, the output power is significantly improved at higher shape transition temperatures of SMPs (the transition temperature is assumed to be 70, 90, 120, 150 and 180°C). Thus, the simulation is in good agreement with the experimental results reported previously (Ma *et al.*, 2013).

(Take in Figure 1)

However, the frequency of film flipping motion as a function of the saturated water vapour pressure at each substrate temperature indicated an exponential correlation, not a linear one. Moreover, an exponential expression is employed to fitting the experimental data as shown in the Figure 2. It should be noted that the values of the parameters y_o, A_1 and t_1 can be adjusted without affecting the others in the exponential equation. Therefore, we substantiate that the frequency of film flipping motion and the saturated water vapour pressure indicate an exponential correlation, based on the relaxation law and simulation result, respectively.

(Take in Figure 2)

Furthermore, the effect of cargo on the flipping frequency of the PEE-PPy film was experimentally characterised. The flipping frequency verifies the relaxation law, and an increase in the frequency (***f***) is equivalent to the decrease in the activation energy ($\triangle E_a$). Meanwhile, the decrease in the activation energy is equivalent to the stored mechanical energy that has a relationship with the transport cargo (σ) and the strain (ε) (along the transport cargo direction) as $\triangle E_a = \sigma\varepsilon$. Therefore, the flipping frequency verifies the modified relaxation law,

$$f_o/f = \exp\left[\left(\sigma \cdot \varepsilon\right)/RT\right] \tag{6}$$

The applicability of this equation can be verified by whether the equation remains balanced when the flipping frequency is increased or decreased and whether a decrease in the flipping frequency (*f*) causes an equivalent increase in the right-hand-side of the modified relaxation equation, therefore increasing the transport cargo, while the strain (ε) and temperature (T) are kept constant. The experimental data of flipping frequency as a function of cargo of the PEE-PPy film were compared to the analytical predictions from Equation 6 as shown in Figure 3. As can be seen, the simulation by relaxation law is in good agreement with the experimental results, where $y_o=2.40876\pm0.2507$, $A_1=5.93602\pm0.42476$ and $t_1=1.92413\pm0.37177$ for the relationship of flipping frequency and cargo. Meanwhile, the exponential equation could also verify the accuracy of the relaxation law for predicting the correlation of flipping frequency and cargo. Based on the nature of the fitted curve, it was considered that the applicability of the exponential equation for fitting the experimental data was verified.

(Take in Figure 3)

Tool-Narayanaswamy equation for SME

During the isothermal annealing of the SMP, when the temperature reaches different levels of enthalpy, the glass transition of polymer is characterised by "fictive temperatures", T_f. The T_f is related to a transition temperature that corresponds to an appropriate cooling rate. The kinetics of annealing to lower and higher enthalpies (fictive temperatures) is asymmetric, giving one of several indications that a single internal parameter is insufficient to describe a given state. An empirical fit of this asymmetry is given by the so-called Tool-Narayanaswamy equation,

$$\tau = \tau_0 \exp\left[\left(x\Delta E_a\right)/\left(RT\right) + \left(1-x\right)\Delta E_a/\left(RT_f\right)\right] \tag{7}$$

where $0 \leqslant x \leqslant 1$ is the nonlinearity parameter. As T_f approaches T, equilibrium is reached and τ follows an Arrhenius expression. Approaching the enthalpy of a given T_f from higher values, after quenching to temperatures lower than T_f, the parameter x increases with time. Approaching the enthalpy of T_f from a lower enthalpy, after rapid heating to temperatures higher than T_f, x decreases with time. Submitting Equation 2 into 7, we have

$$f_0/f = \exp\left[\left(x\Delta E_a\right)/\left(RT\right) + \left(1-x\right)\Delta E_a/\left(RT_f\right)\right] \tag{8}$$

Combining Equations 7 and 8, the effect of saturated water vapour pressure on the flipping frequency can be written as,

$$f_0/f = \exp\left[\left(x\left(\Delta E_\mathrm{a} - PV\right)\right)/\left(RT\right) + \left(1-x\right)\left(\Delta E_\mathrm{a} - PV\right)/\left(RT_\mathrm{f}\right)\right] \tag{9}$$

(Take in Figure 4)

The simulation of Equation 7 was compared to that of Equation 5 in order to characterise the effect of ***x*** and ***T*f** on the ***f*0/*f***, respectively. Figures 4(a) and 4(b) plot numerical results for frequency (***f*0/*f***) with output power at different values of ***T*f/*T*** and ***x***, respectively. It can be seen from Figure 4 that, with an increase in the nonlinearity parameter (***x***), the frequency of the film flipping motion decreases. On the other hand, the frequency of film flipping motion decreases with an increase in the ***T*f/*T***. As indicated by Equation 9, the decrease in the frequency of film flipping motion has two contributors, namely a synergistic effect of ***T*f/*T*** and ***x***, as can be seen in Equations 10 and 11.

$$f_0/f = \exp\left[x_0\left(\Delta E_\mathrm{a} - PV\right)/\left(RT_\mathrm{f0}\right) + x_1\left(\Delta E_\mathrm{a} - PV\right)/\left(RT_\mathrm{f1}\right) + x_2\left(\Delta E_\mathrm{a} - PV\right)/\left(RT_\mathrm{f2}\right) + \ldots\right] \tag{10}$$

$$f_0/f = \exp\sum_{i=0}^{M} x_i\left(\Delta E_\mathrm{a} - PV\right)/RT_\mathrm{fi} \tag{11}$$

where ***T*f0** is the initial temperature that is assumed to be equal to that of the environment, ***T***. It is assumed that the polymer consists of multi-transition segments, where *M*=∞. Thus, we have the limit expression of the Equation 11 to be,

$$f_0/f = \frac{\left(\Delta E_\mathrm{a} - PV\right)}{R}\cdot\frac{1}{M\cdot T}\left(\frac{1}{1-a}\right) \tag{12}$$

where ***M*** presents the number of multi-components or phases in SMPs and ***a*** is ratio of ***T*f/*T***, ***T*f2/*T*f1**, ***T*f3/*T*f2**. Therefore, the correlation of frequency and stored mechanical energy can be plotted as shown in Figure 5.

(Take in Figure 5)

Furthermore, the effect of cargo on the flipping frequency of SMPs was also further characterised by submitting Equation 4 into Equation 9 to give,

$$f_0/f = \exp\left[\frac{\left(\sigma\cdot\varepsilon\right)}{R}\left(\frac{x_0}{T_\mathrm{f0}} + \frac{x_1}{T_\mathrm{f1}} + \frac{x_2}{T_\mathrm{f2}} + \ldots\ldots + \frac{x_i}{T_\mathrm{fi}}\right)\right] = \sum_{i=0}^{M}\exp\frac{\left(\sigma\cdot\varepsilon\right)}{R}\left(\frac{x_i}{T_\mathrm{fi}}\right) \tag{13}$$

Figures 6(a) and 6(b) plot numerical results for frequency (f_0/f) with cargo at different values of x and T_f, respectively. It can be seen from Figure 6 that, with an increase in the nonlinearity parameter (x), the frequency of film flipping motion decreases. On the other hand, the frequency of film flipping motion decreases with an increase in the temperature T_f approaching to T. As indicated by Equation 13, the decrease in frequency of film flipping motion also has two contributors, namely the synergistic effect of x and T_f.

(Take in Figure 6)

Tool-Narayanaswamy equation for temperature memorisation

It was found that the carbon nanotubes (CNTs) in polyvinyl alcohol (PVA) composite nanotube fibres induced an SME and temperature memory with a peak of recovery stress at the temperature of their initial deformation (Miaudet *et al.*, 2007). The temperature corresponding to the maximum recovery stress in constrained recovery is roughly the temperature at which the pre-deformation occurs, known as the temperature memory effect (TME) in SMPs (Sun and Huang, 2010). The TME in PEE-PPy films was also characterised by the maximum recovery stress roughly remaining constant in the bio-inspired cyclic recovery driven by water gradients, as shown by the experimental results of stress as a function of time (Miaudet *et al.*, 2007). By combining the relaxation law and experimental base of Pierre Miaudet *et al.* (2007), we are able to provide a further clarification on the theoretical mechanism, which is a challenging problem. Such a clarification will significantly enhance the understanding of these theoretical and experimental features of PEE-PPy films.

Based on the relaxation theory and the thermodynamics of polymers, the correlation of stress generated by the SMP composite and temperature could be qualitatively depicted, when it is reheated at a fixed strain. Here, the relaxation theory and the Arrhenius equation are introduced to qualitatively depict the correlation of constraint stress and temperature for the polymer in a glassy state,

$$\tau = \tau_{\mathrm{o}} \exp\left(\frac{\Delta E_{\mathrm{a}} - a\sigma}{RT}\right) \tag{14}$$

where the parameters a and σ are the same as those in Equation 6. Equation 14 has been widely used to study the effect of applied mechanical stress on the transition temperature of polymers in a glassy state (He *et al.*, 1999). Equation 14 argues that the temperature increase is equivalent to the decrease in the $\triangle E_a - a\sigma$ part in terms of accelerating the recovery time, where the latter part is determined by the stored mechanical energy ($\triangle E_a$) and applied mechanical stress (σ). As the stored mechanical energy is kept constant, the temperature increase could be equivalent to the stress increase to ensure that the latter part ($\triangle E_a - \alpha\ \sigma$) decreases. Therefore, the stress generated by SMP composite is gradually increased as the temperature increases up to T_s [79.1°C, 94.6°C, 122.8°C, 155.0°C and 187.3°C, respectively, for each of the different colour curves (Miaudet *et al.*, 2007)] that is the temperature corresponding to the maximum stress, as shown in Figure 3. It should be noted that the T_s is shifted to the right resulting from the relaxation. Furthermore, the stress is altered as a function of strain, as described by Equation 15 (Liu and Gall, 2006),

$$\sigma^{o} = \left(1+\varepsilon\right)\sigma \tag{15}$$

where σ^0 is the true stress, and ε is the strain. Here, $\varepsilon \leqslant 0$ as a result of the fibre recovering from the initial 800% deformation. Therefore, the true stress σ^0 gradually decreases while the parameter $(1+\varepsilon)$ decreases, prior to the temperature being reaching above the peak temperature level (T_s), where the polymer is in glassy state.

However, such a correlation of stress and temperature just depicts the behaviour of SMP composite that is in the glassy state (where $T \leqslant T_s$), where the stored mechanical energy ($\triangle E_a$) and material constant (a) are taken as constants. Consequently, it would be useful to correlate the stress and temperature for SMP composite at temperatures above the T_s (where $T \geqslant T_s$). Based on the thermodynamics of polymers and the experimental results of dynamic mechanical analysis, it was considered that the elastic modulus (E) of SMP composite should gradually decrease as the temperature increased (Miaudet *et al.*, 2007; Sun and Huang, 2010; Casalini and Roland, 2004; Bässler, 1987; Haward, 1972; He *et al.*, 1999; Liu and Gall, 2006). SMPs generally can retain two, or sometimes more than three, shapes, and the transition in shapes can be induced by temperature increase. Heating up the SMP above a transition temperature induces the SME. The characterisation of the transition temperature, including glass transition temperature (T_g) or melting transition temperature (T_m), is critical and essential for SMPs. In previous studies, thermomechanical behaviours of SMPs were investigated under isothermal, constrained cooling and heating conditions (Yakacki and Shandas, 2007; Francisco *et al.*, 2010). However, as the temperature traverses the material's T_g, more complex behaviours are exhibited. Therefore, it is critical to investigate the frequency dependence of SMP thermomechanical behaviour during programmed and constrained recovery in order to characterise the relaxation behaviour of SMPs (Razzaq *et al.*, 2007). Due to the nature of the kinetics of glass transition, SMPs obey the relaxation rule, and the glass transition of polymeric materials exhibits relaxation behaviour. Such phenomena can also be used to account for the $\boldsymbol{T}_\mathrm{s}$ being roughly (not completely) equal to the deformation temperature ($\boldsymbol{T}_\mathrm{d}$). Therefore, the correlation between $\boldsymbol{T}_\mathrm{g}$ and frequency can be depicted as follows (Liu and Gall, 2006),

$$f_0/f = \exp\left[\frac{\Delta E_\mathrm{a}}{RT_\mathrm{g}}\left(x + (1-x)\frac{T_\mathrm{g}}{T_\mathrm{f}}\right)\right] \qquad (16)$$

(Take in Figure 7)

In comparison with the experimental results reported in previous study (Razzaq *et al.*, 2007), Figures 7(a) and 7(b) plot numerical results for frequency (f_0/f) with $\boldsymbol{T}_\mathrm{g}$ of SMP at different values of x and $\boldsymbol{T}_\mathrm{f}$, respectively. It can be seen, from Figure 7, that with an increase in the nonlinearity parameter (x), the $\boldsymbol{T}_\mathrm{g}$ gradually increases at the same frequency of SMP. On the other hand, the $\boldsymbol{T}_\mathrm{g}$ is seen to also increase with the increase in $\boldsymbol{T}_\mathrm{f}$, approaching to $\boldsymbol{T}$ at the same frequency of SMP. As indicated by Equation 16, the change in $\boldsymbol{T}_\mathrm{g}$ of SMP has two contributors, namely a synergistic effect of x and $\boldsymbol{T}_\mathrm{f}$. In comparison with previous experimental results, it is supported that the applicability of Tool-Narayanaswamy equation for the SMPs of which the molecules are incorporated with more than two segments or domains. Furthermore, it can be seen that the transition temperature of SMPs is roughly the temperature at which the pre-deformation is conducted. In other words, the TME is determined by or indirectly determined by the transition temperature. Therefore, it is clear that the Tool-Narayanaswamy equation is capable of providing an accurate prediction of SME and TME.

Conclusions

The study reported here focused on understanding the mechanisms underpinning thermo-mechanical features such as SME and TME that had been observed in SMPs. On the origin of relaxation theory and Tool-Narayanaswamy equation, a phenomenological and quantitative approach has been presented to correlate the relaxation time, constraint stress, recovery strength, and transition temperature with frequency, as well as the recovery stress and temperature, for SMPs. Further clarification on the theoretical mechanism, which is a challenging problem for SMPs, has also been provided. The outcome of this study is also expected to help the exploration of the working mechanism underpinning the experimental (or phenomenal) results and significantly enhance understanding of such experimental observations/materials behavioural features reported previously.

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Figure 1 Numerical results for the frequency as a function of output power of the PEE-PPy film, *T*=70, 90, 120, 150 and 180°C

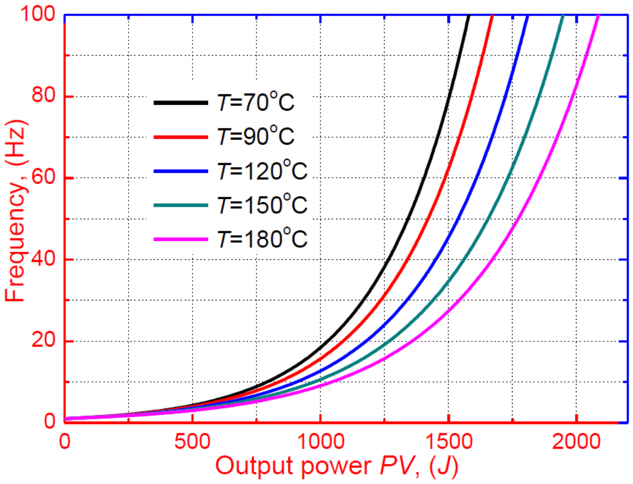

Figure 2 Frequency of film flipping motion as a function of saturated water vapour pressure of the PEE-PPy film, comparison of experimental results (from Ma *et al.*, 2013) with simulation results of the fitting exponential Equation 5

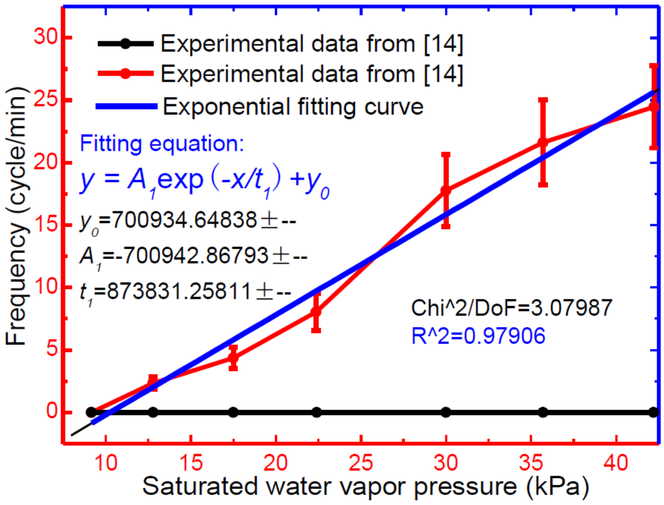

Figure 3 Frequency of film flipping motion as a function of the cargo of the PEE-PPy film, comparison of experimental results (from Ma *et al.*, 2013) with simulation results of the fitting exponential Equation 8

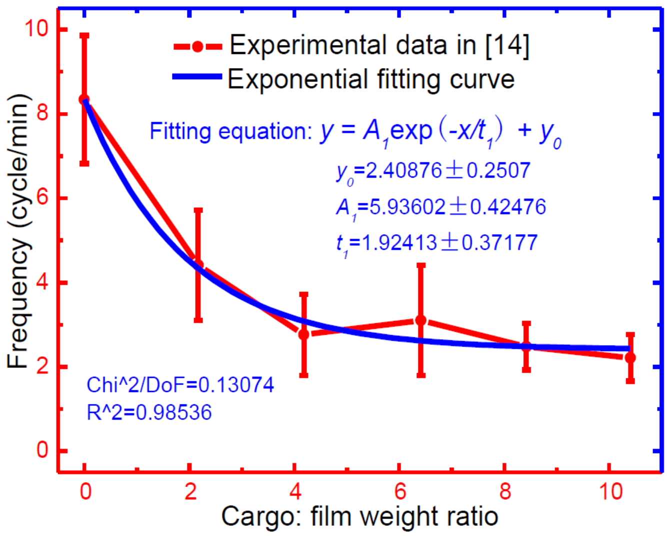

Figure 4 Numerical results for the frequency as a function of output power of the PEE-PPy film, (a) T_f/T=0.9, 0.8, 0.7, 0.6 and 0.5; (b) x=0.00, 0.25, 0.50, 0.75 and 1.0

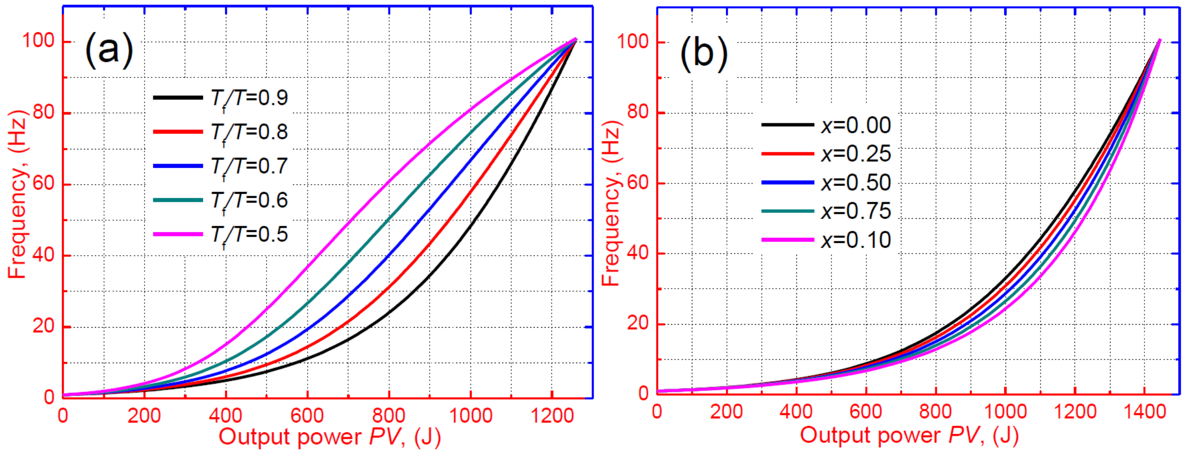

Figure 5 Numerical results for the frequency as a function of output power of the PEE-PPy film, (a) M=2, 3, 4, 5 and 6; (b) a =0.95, 0.90, 0.85, 0.80 and 0.75

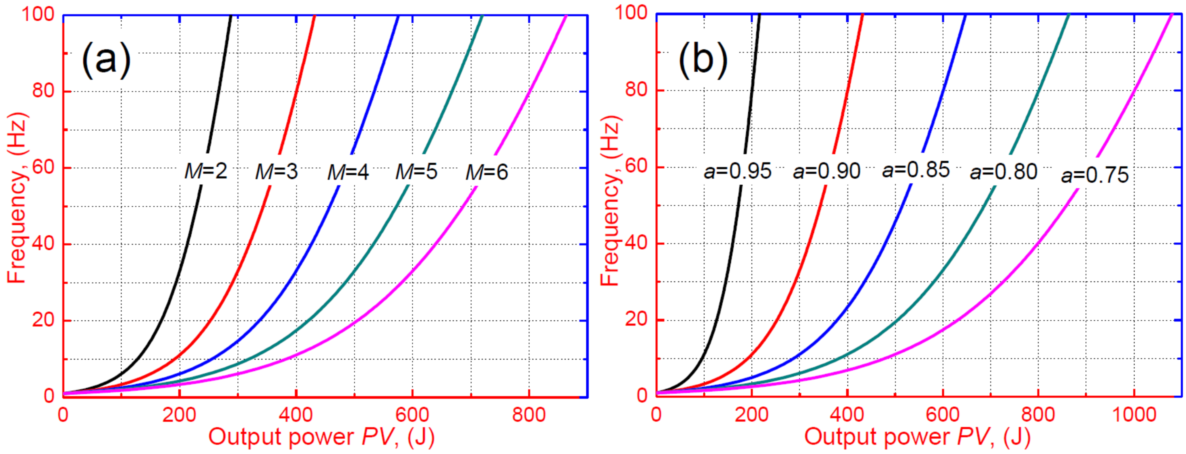

Figure 6 Numerical results for the frequency as a function of cargo of the PEE-PPy film, (a) x=0.0, 0.2, 0.4, 0.6, 0.8 and 1.0, where T_f =0.9T; (b) T_f =T, T_f =0.8T, T_f =0.6T, T_f=0.4T and T_f =0.2T, where x=0.5

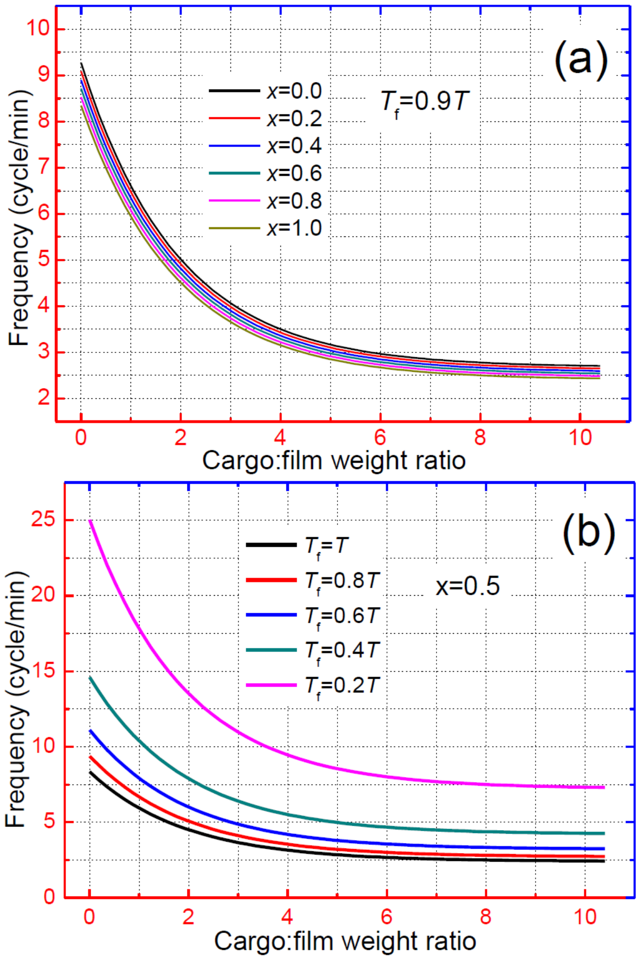

Figure 7 Numerical results for the frequency as a function of glass transition temperature compared with the previous experimental data of Razzaq *et al*. (2007), (a) *x*=0.0 and 1.0, where T_f =0.9T; (b) T_f =0.6T and T_f = T, where *x*=0.5