Nearly constant dielectric loss behavior in poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) biodegradable polyester

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The measurement of dielectric spectroscopy over a broad frequency range of $0.01–10^7$ Hz has been conducted to examine the segmental motions in poly[3-hydroxybutyrate-*co*-3-hydroxyvalerate] (PHBV) biopolymers. The ac conductivity at either low temperatures or high frequencies is almost temperature independent, indicating clearly that the nearly constant loss (NCL) phenomenon also takes place in polymers. The respective data were analyzed by adding a NCL term to the Jonscher relation. NCL in PHBV is discussed to be originated from the vibrational motion model. PHBV may have potential application as a biodegradable dielectric material. © 2009 American Institute of Physics. [DOI: 10.1063/1.3125271]

The frequency-dependent electrical behavior of disordered materials (such as glasses and highly doped crystals) shows surprising simplicities involving two regions of universalities. The universal behavior of disordered material was observed in mechanical relaxation experiments a long time ago.[1] On one hand, at relatively high temperatures and/or low frequencies, the following "universal dielectric response" (UDR) prevails with a power law behavior on the real part of the complex conductivity $\sigma'(f)$,

$$\sigma'(f) = \sigma_{\mathrm{dc}} + \sigma_0 f^n, \quad 0 < n < 1, \tag{1}$$

where f is frequency and the exponent n falls in a typical range of 0.5–0.7 for ionic conductors.[2] On the other hand, at sufficiently low temperatures and/or high frequencies, the frequency response of $\sigma'(f)$ depends linearly or nearly linearly on frequency.[3–5] In a double logarithmic figure of σ' versus f, the slope of the curve $\log(\sigma')/\log(f)$ approaches 1, implying a negligible frequency dependence of the imaginary part of dielectric permittivity, $\varepsilon''(f) = \sigma'(f)/2\pi f$. Naturally, this type of frequency response is called nearly constant loss (NCL).[3–5] Its frequency dependence is given by

$$\sigma'_{\mathrm{NCL}}(f) = 2\pi f \varepsilon''_{\mathrm{NCL}}(f) \approx A f^{1-a}, \tag{2}$$

$$\varepsilon''_{\mathrm{NCL}}(f) \approx \frac{A}{2\pi} f^{-a}, \tag{3}$$

where a is positive but nearly equal to zero and A is a constant with weak temperature dependence.[6] In the whole frequency range, for almost all thermally activated hopping processes that involve both ions and electrons in either crystalline or amorphous materials, the ac conductivity can be well approximated as

$$\sigma'(f) \approx \sigma_{\mathrm{dc}} + \sigma_0 f^n + A f. \tag{4}$$

Current interpretations of the frequency-dependent behavior of the NCL regime remain more speculative. There is no unambiguous explanation to distinguish whether the NCL is caused by vibrational motion[5] or by correlated localized displacements of charged entities.[7]

Biodegradable copolymers poly[3-hydroxybutyrate-*co*-3-hydroxyvalerate] (PHBV) of poly[3-hydroxybutyrate] and poly[3-hydroxyvalerate] can be produced by microbial fermentation[8] and are available commercially. Their use in drug release systems has been reported in recent years.[9] Due to the unique physicochemical properties of these biodegradable and biocompatible polyesters (such as piezoelectricity,[10] a property claimed to induce bone reformation on load-bearing sites), they are regarded as special materials and are at the center of a growing interest in various fields of science.[11,12] The piezoelectric coefficient of PHBV is compatible with bone and keratin.[13] Ando and Fukada[10] and Ando *et al.*[14] reported a piezoelectric relaxation phenomenon around the glass transition temperature of PHBV. It is presumably caused by the related dielectric and flexibility relaxations.[15] However, there are really sparse dielectric studies reported on PHBV. In this letter, the measurements of ac conductivity and dielectric permittivity of PHBV are reported. Particularly, the contribution to ac conductivity from nearly constant dielectric loss has been observed in a pure biopolymer.

PHBV powder (polyhydroxyvalerate 8% grade: D 400P, purchased from ICI) was dissolved in chloroform at 80 °C at a concentration of 60 mg/ml, a known volume of which was cast on glass plate. After conditioned for 2 days at room temperature, the film was further dried under vacuum at 60 °C to remove the residual chloroform. The PHBV film with thickness of 0.15 mm was obtained and cut into 10×10 mm^2 pieces. The PHBV films were then washed with acetone and dried before use. The chemical structure of PHBV, as shown in the inset of Fig. 1, is

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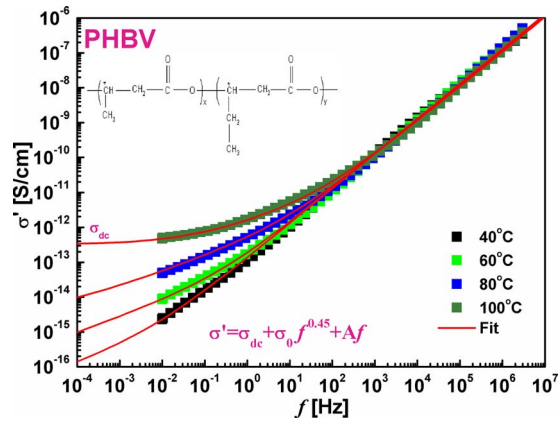b)Electronic mail: psliren@scut.edu.cn.

FIG. 1. (Color online) Frequency dependence of conductivity at various temperatures for PHBV biopolymers. The solid lines are fit of experimental data using Eq. (4). The inset shows the chemical structure of PHBV.

[–O–CH(CH$_3$)–CH$_2$–CO–] for hydroxybutyrate and [–O–CH(C$_2$H$_5$)–CH$_2$–CO–] for hydroxyvalerate (HV). For electrical measurement, different types of contacts (Au and Ag) are sputtered on both surfaces. The dielectric properties and ac conductivity were measured by using a broadband frequency-response analyzer (Novocontrol Alpha analyzer) over a broad frequency range (0.01 Hz–10 MHz) at various temperatures.

Figure 1 shows the variation in ac conductivity σ' with frequency at various temperatures for PHBV films with Au contact. At high temperatures (100 °C), the log-log curves are flat in the low frequency region as the conductivity values approach those of σ_{dc}. As the frequency increases, the curves become dispersive and can be parametrized using the UDR power law with exponential $n < 1$. With further increase in frequency, the conductivity becomes almost independent of temperature and displays a linear relationship. The span of the linear regime becomes bigger and bigger with decreasing temperature. This is also shown in the inset of Fig. 2 where $\varepsilon''(f)$ is plotted against frequency for PHBV. At high frequency, the data at different temperatures collapse onto almost a single curve, revealing that ε'' is independent of frequency and therefore a genuine NCL behavior. This

phenomenon is usually observed in glasses and ceramics. Natesan *et al.*[16] recently reported this behavior in (PEO-LiClO$_4$) polymer electrolyte. In order to accommodate this contribution, a linear term in frequency has been introduced to describe the ac conductivity of disordered systems by a superposition of a Jonscher term and a NCL term of the form, as shown in Eq. (4). We extended this approach to polymer ion conducting systems to verify the universality of this approach in all forms of ionic conductors. We fitted the ac conductivity data using Eq. (4). It is evident from Fig. 1 that the ac conductivity data were described reasonably well by Eq. (4).

At all fitting temperatures, the exponent n for UDR is fixed at 0.45, i.e., n is kept independent of temperature. The UDR behavior in PHBV indicates a hopping transport of localized charge carriers. The temperature independence of the exponent n of PHBV is very similar to that of ion conductors.[3,17] It is evident from the ac conductivity spectrum of PHBV that below the glass transition temperature $T_g \approx 15$ °C,[10,13,14] the conductivity is almost independent of temperature; while above T_g, the conductivity in the UDR regime increases with increasing temperatures and remains independent of temperature in the NCL regime. This observation reveals that the low frequency transport is much coupled to the segmental motion of polymer chains since below T_g, the segmental motion is frozen and above T_g the segmental mobility sets in and thereby moves more freely. This analysis clearly indicates that there exists a crossover from NCL to the fractional power law dependent hopping conductivity. Specifically, it provides evidence that the NCL in PHBV is most likely caused by the vibrational motion model.[5]

As shown in Fig. 2, at lower frequencies $\varepsilon''(f)$ decreases rapidly with increasing frequencies, which was attributed to the interfacial polarization effect between the contact electrode and PHBV. The dielectric constant measured with Ag electrodes (dielectric data not shown here) is relatively smaller than that with Au ones, which also confirms the interfacial polarization effect. Above 100 Hz, the dielectric permittivity of PHBV is dominated by the NCL behavior, as can be seen by the guided lines (dotted lines) in Fig. 2. From the Kramers–Kronig relation,[3] the power law of ac conductivity (f^m) would lead to a real part of dielectric permittivity satisfying $\varepsilon' = Bf^{m-1}$. Then we have,

$$f\varepsilon' = Bf^m. \tag{5}$$

Therefore, at a given temperature, a straight line with a slope of m should be obtained in a $\log(f\varepsilon')$ versus $\log(f)$ plot. Such a plot of PHBV at selected temperature is shown in Fig. 3. Surprisingly, it can be observed that experimental data fit Eq. (5) quite well throughout the whole frequency range at all measurement temperatures. While from Fig. 1, it can be seen that the power law of the ac conductivity is only valid at high frequencies, especially at high temperatures.

We fitted all the $f\varepsilon'$ data using Eq. (5). As can be seen from the inset of Fig. 3, the exponent m is very close to unity and decreases only slightly with increasing temperatures. Since the exponent m is close to the exponent of NCL, the apparent discrepancy of the results in Figs. 1 and 3 can be
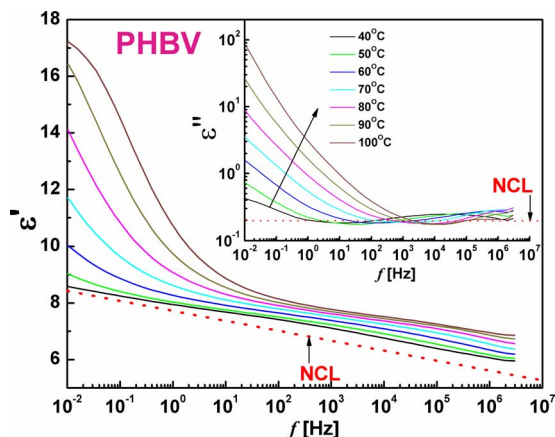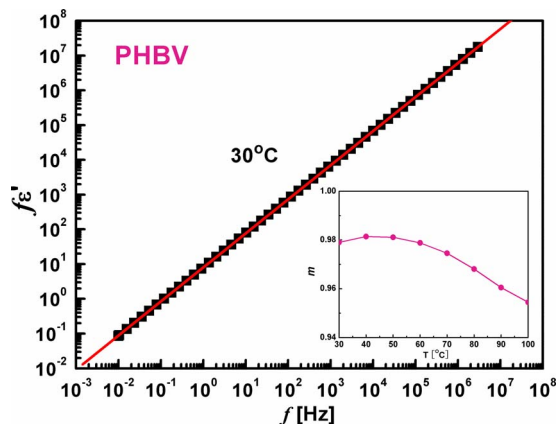

FIG. 2. (Color online) Frequency dependence of dielectric permittivity at various temperatures for PHBV biopolymers. The dotted lines are a guide to the eyes.

FIG. 3. (Color online) Plot of $f\varepsilon'$ against f for PHBV at 30 °C. The solid lines are the best fitted lines according to Eq. (5). The inset displays the temperature dependence of the exponent m.

attributed to the greater contribution to ε' from NCL than that from UDR in PHBV. With increasing temperature, the contribution from UDR also increases and it leads to a continuous decrease in m. So the combination of UDR and NCL describes well the dynamics of segmental molecular motion in the polymers. For conducting materials, UDR is commonly ascribed to the hopping of Anderson-localized charge carriers. However, the origin of NCL behavior is still not well understood and remains controversial. Ngai and Casalini[6] pointed out that NCL in ionic conductors originates from the vibrational relaxation of the ions in very slowly decaying anharmonic cages. Another viewpoint is that NCL originates from the motion of a group of atoms in asymmetric double well potential configurations.[7] NCL has also been attributed to the hopping movements of mobile ions between neighboring sites.[18,19] Based on the ac conductivity study, we propose that NCL in PHBV most likely originates from the vibrational relaxation of the polymer chains.

It should be noted that a piezoelectric relaxation phenomenon above the glass transition temperature of PHBV has been reported.[13,14] It was presumably caused by the related dielectric and flexibility relaxation.[15] In the present study, NCL behavior of PHBV is also observed in this temperature range, which dominates the dielectric relaxation in PHBV. Therefore, a study of the NCL behavior is very important to understand the glass transition and piezoelectric relaxation phenomenon in PHBV. Actually, similar studies in various types of materials (ceramic, glassy and polymers,

etc.) are needed in order to gain further insights about the origin of NCL phenomenon itself.

In summary, we have investigated the temperature and frequency dependence of ac conductivity and dielectric spectra of PHBV (8% HV) biodegradable insulating polymers. Universal power law (UDR) and NCL behavior were found in PHBV. The contribution to ε' from NCL is much larger than that from UDR, so the dielectric constant of PHBV could be described by a different power law relation. Since PHBV is biodegradable and environmentally friendly, it may find its application as a "green" dielectric material.

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