

Role of epoxidation on segmental motion of polyisoprene as studied by broadband dielectric spectroscopy

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ABSTRACT: In this article, the broadband dielectric spectroscopy (BDS) is used to investigate the relaxation behavior of polyisoprene (PI) epoxidized to various levels and the special consideration is devoted to the effect of epoxidation degree on segmental relaxation. To associate segmental relaxation with molecular structure, several empirical equations are used to fit experimental data. Furthermore, we want to discuss the origin of the change of segmental relaxation. Thermal measurement reveals that glass transition temperature of epoxidized PI (EPI) increase with the increase of epoxidation degrees. The epoxidation modification increases the breadth of the dielectric dispersion. Oxirane groups as steric interference enhance the cooperativity of segmental relaxation process and retard the relaxation process, which results in the increase of coupling parameter. Specifically, Vogel–Fulcher–Tammann equation shows the relationship between correlation length and temperature. These results further illustrate the effect of epoxidation group on segmental motion of PI. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43879.

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INTRODUCTION

Epoxidation is a very useful chemical reaction, because it makes polymer bear polar groups and markedly changes some properties of polymer such as gas permeability,¹ self-healing,² and compatibility with the polymer bearing polar groups.³ Many previous articles focused on the preparation and properties of epoxidized polyisoprene (EPI).^{4–6} Figure 1 shows the chemical structure of polyisoprene (PI) repeat unit and the oxirane moiety resulting from epoxidation. It is well known that the stereospecific epoxidation reaction makes PI bear epoxide groups randomly distributed along the polymer backbone. This polar chemical structure of polymer chain usually has a profound influence on its relaxation behavior. In present work, our group makes systematic investigation on how epoxidation affects the molecular dynamics of PI. In addition, a new phenomenon that PI exhibits the stronger temperature dependence of relaxation time (τ), compared with the temperature dependence of τ for epoxidized PI (EPI) is observed by us.

To my knowledge, few researches focus on the dynamics of EPI from molecular level, although the physical properties of EPI are reported by many researchers. Broadband dielectric spectroscopy (BDS) is often believed to be a powerful tool for the investigation of molecular dynamics of polymer. When polymer is placed in an electric field, it is subjected to dipole polarization.

These polarization mechanisms have considerable different time and length scales, making BDS suited for the study of polymer dynamics. Different motional processes taking place on different time scales can be investigated in a broad frequency and temperature range. In addition, BDS analysis of polymer contributes to a better understanding of the structure and property relationship at the molecular level. Supramolecular relaxation,⁷ polymer structure,^{8,9} polymeric different motion modes,^{10–17} and polymer nanocomposite^{18–20} have been studied by BDS. It is notable that the dynamics of PI chains has attracted many authors' attention.^{21–26} In PI chains, molecular dipole moment perpendicular to the chain skeleton causes segmental motion (SM) and the dipole moment parallel to the chain contour results in normal motion (NM). Such fact indicates that SM and NM can be both observed in PI. Furthermore, previous works found that both temperature dependences of these two modes decoupled from each other near the glass transition, which means that the temperature dependences of the two length scales are different. This anomalous dielectric relaxation phenomenon indicated that SM and NM cannot be described by the same friction coefficient near the glass transition. To enlighten these results from a more microscopic point of view, Schonhals developed the conception that SM as a cooperative process can be characterized by the correlation length (ξ).^{11,15,27} The ξ for SM is approximately equal to the mean square end-



Figure 1. Repeat unit of PI (left) and that of EPI (right).

Table I. EPI of Various Epoxidation Degrees

Sample	Epoxidation degree (mol %, based on isoprene units)	MCPBA (g)
EPI-5	5	3.05
EPI-10	10	6.10
EPI-20	20	12.20
EPI-30	30	18.30
EPI-50	50	30.50

to-end distance ($\langle R^2 \rangle$) of the polymer chain, which is described by¹¹

$$\xi \approx \langle R^2 \rangle^{1/2} \quad (1)$$

Here, we consider the change of ξ as the reason why segmental relaxation is affected by epoxidation. To investigate the segmental relaxation mechanism influenced by epoxidation, differential scanning calorimetry (DSC) and BDS are used to observe glass transition temperature (T_g) and the dynamics of segmental motion, respectively. Near the glass transition temperature, polymer usually exhibits a dispersion in their dielectric response. Such segmental relaxation cannot be represented as a single Debye process and the relaxation functions of that are invariably nonexponential. Therefore, several empirical equations are used to analyze experimental data to help us understand the origin of the change of segmental relaxation.

EXPERIMENTAL

Materials

PI (GPC data: $M_n = 241468$, $DPI = 3.893$) was purchased from Shanghai Sanlian. 3-Chloroperoxybenzoic acid (MCPBA, 85%) was purchased from Adamas Reagent. Tetrahydrofuran (THF) was purchased from Shanghai Titan Scientific and used without further purification.

Synthesis of EPI

The epoxidation reaction was performed according to the previous literature.^{28–30} In a 1 L one-neck round-bottom flask equipped with magnetic stirrer, 20.4 g of PI (0.3 mol isoprene units) was first dissolved in 450 mL of THF. A solution of MCPBA in 50 mL of THF was added dropwise at room temperature into the PI solution at such rate that the MCPBA solution was added completely after 1 h. The reaction mixture was then further stirred for another 5 h. Afterward the EPI solution was added into methanol for precipitation and then dried at 50 °C under vacuum for 2 days. The details of EPI were summarized in Table I. The epoxidation modification of PI was shown in Figure 2.

Measurements and Characterization

Fourier Transform Infrared (FTIR). Fourier Transform Infrared (FTIR) spectra of all samples were measured at room temperature using Thermo Scientific Nicolet iS50 FTIR with a resolution of 4 cm^{-1} . The wavenumber range was from 4000 to 650 cm^{-1} .

DSC. The T_g of all samples was performed on TA instrument Q200 series under a nitrogen atmosphere at a heating rate of 5 °C/min and the weights of all samples were in the range of 6–8 mg. Heat calibration is used in our laboratory. The temperature range was from –70 °C to 0 °C.

BDS. Dielectric measurements were performed over the frequency range of 10^{-1} – 10^7 Hz on a Novocontrol Concept 50 system with Alpha impedance analyzer and Quatro Cryosystem temperature control. The disk-shaped film of about 1 mm thickness was placed between two parallel electrodes with 20 mm diameter. The temperature range was from –70 °C to 50 °C in steps of 10 °C.

RESULTS AND DISCUSSION

Molecular Structure and T_g

To study the segmental relaxation mechanism influenced by epoxidation, we choose PI and EPI as research objective. The

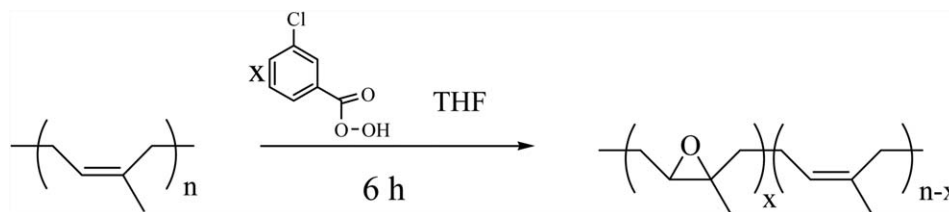


Figure 2. Synthesis of different epoxidation degrees EPI.

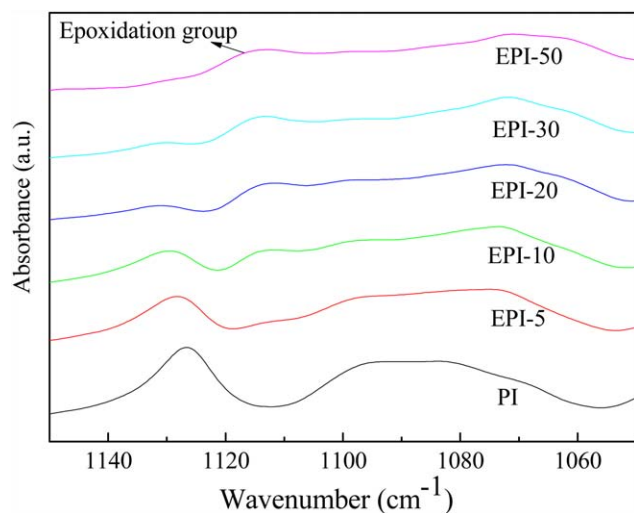


Figure 3. FTIR spectra of PI and EPI with different epoxidation degrees. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EPI samples with different epoxidation degrees are prepared by MCPBA. The appearance of C–O–C is confirmed by the characteristic band at 1114 cm^{-1} on the FTIR spectra, as shown in Figure 3. However, EPI-5 does not exhibit obvious characteristic peak at 1114 cm^{-1} . With the increase of epoxidation degree, the intensity of characteristic band increases. Such phenomenon suggests that epoxidation group is introduced into PI chains.

A single glass transition is observed for all samples, as presented in Figure 4. DSC at a scanning of 5 °C/min reveals the T_g of PI at -63 °C , EPI-5 at -61 °C , EPI-10 at -53 °C , EPI-20 at -45 °C , EPI-30 at -37 °C , and EPI-50 at -22 °C . Meanwhile, EPI-50 shows the highest T_g among all samples. The changes of T_g may be attributed to molecular motion of PI inhibited by epoxidation.

Dielectric Loss Analysis

Studying the segmental relaxation behavior, we usually consider the two perspectives. In an isolated chain, segmental dynamics

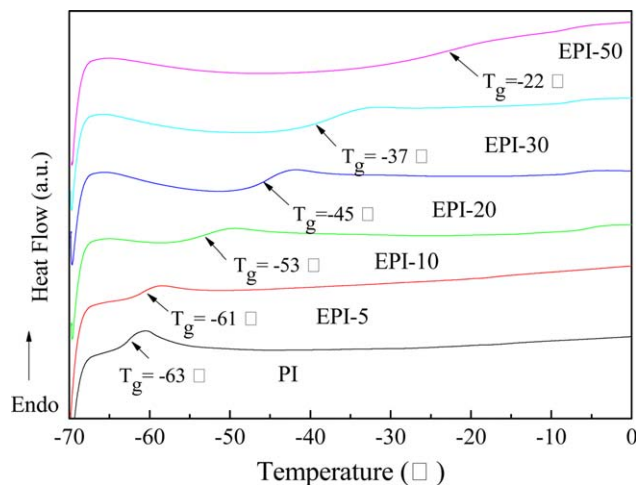


Figure 4. DSC curves obtained for PI and EPI with different epoxidation degrees. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are described in terms of intramolecular correlated bond conformational transition. In dense phase, there exist intermolecular constraint on segmental relaxation in terms of density fluctuation in the local environment.^{31,32}

The dielectric loss (ϵ'') as a function of frequency for neat PI exhibits the well-known characteristic of thermal activated process (segmental relaxation) at temperature ranging from 213 K to 248 K, as shown in Figure 5(a). In each spectrum, a clear loss peak associated with segmental relaxation is observed and this loss peak shifts toward higher frequencies with increasing temperature, which is found in all samples. Additionally, the breadth of normalized ϵ'' dielectric dispersion increases with increasing epoxidation degrees in the vicinity of glass transition region, as shown in Figure 5(b). Polymeric segmental relaxation is the result of cooperative motion of repeat unit of different chains, believed to be a few nanometer size near T_g . The most characteristic feature of segmental relaxation of polymer is a nonexponential behavior and the shape of that is invariably

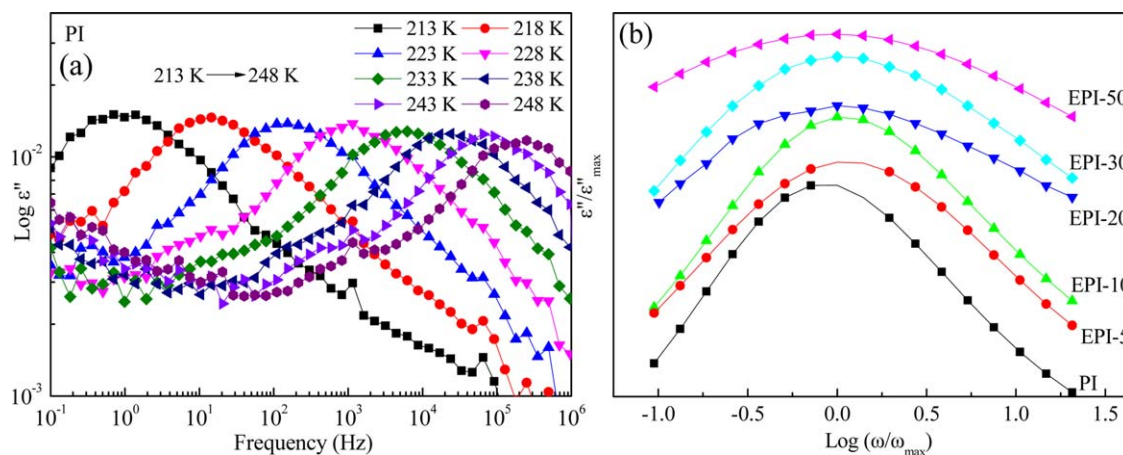


Figure 5. Dielectric loss behavior analysis. (a) Dielectric loss as a function of frequency for neat PI at different temperature range. (b) Superpositioned $\epsilon''/\epsilon''_{\max}$ measured for PI and EPI in the vicinity of their glass transition. The values of ϵ'' are normalized by the maximum in ϵ'' occurring at ω_{\max} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. The Parameters β_{kww} and n for PI and EPI in the Vicinity of Their Glass Transition

	PI	EPI-5	EEPI-10	EPI-20	EPI-30	EPI-50
β_{kww}	0.5093	0.4402	0.3583	0.3574	0.2424	0.230
N	0.4907	0.5598	0.6417	0.6426	0.7576	0.7698

wider than Debye process.^{33,34} The asymmetrically broadened frequency dispersion of the dielectric spectrum, originating from the interactions among repeat units, is fitted by the one-sided Fourier transforms of the Kohlrausch-Williams-Watts (KWW) function^{35,36}:

$$\Phi(t) = \exp\left[-\left(\frac{t}{\tau_{kww}}\right)^{\beta_{kww}}\right] \quad (2)$$

The dependence of β_{kww} on different epoxidation degrees is displayed in Table II. The stretching parameter β_{kww} ($0 < \beta_{kww} \leq 1$) leads to an asymmetric broadening of $\Phi(t)$ at short time. τ_{kww} is the related relaxation time. A smaller β_{kww} is associated with a broader distribution of relaxation time (broader spectrum).

The coupling model has been applied to segmental relaxation research. This model is based on general physical principles to describe relaxation behaviors of the individual relaxing units coupled with each other, which is usually described by

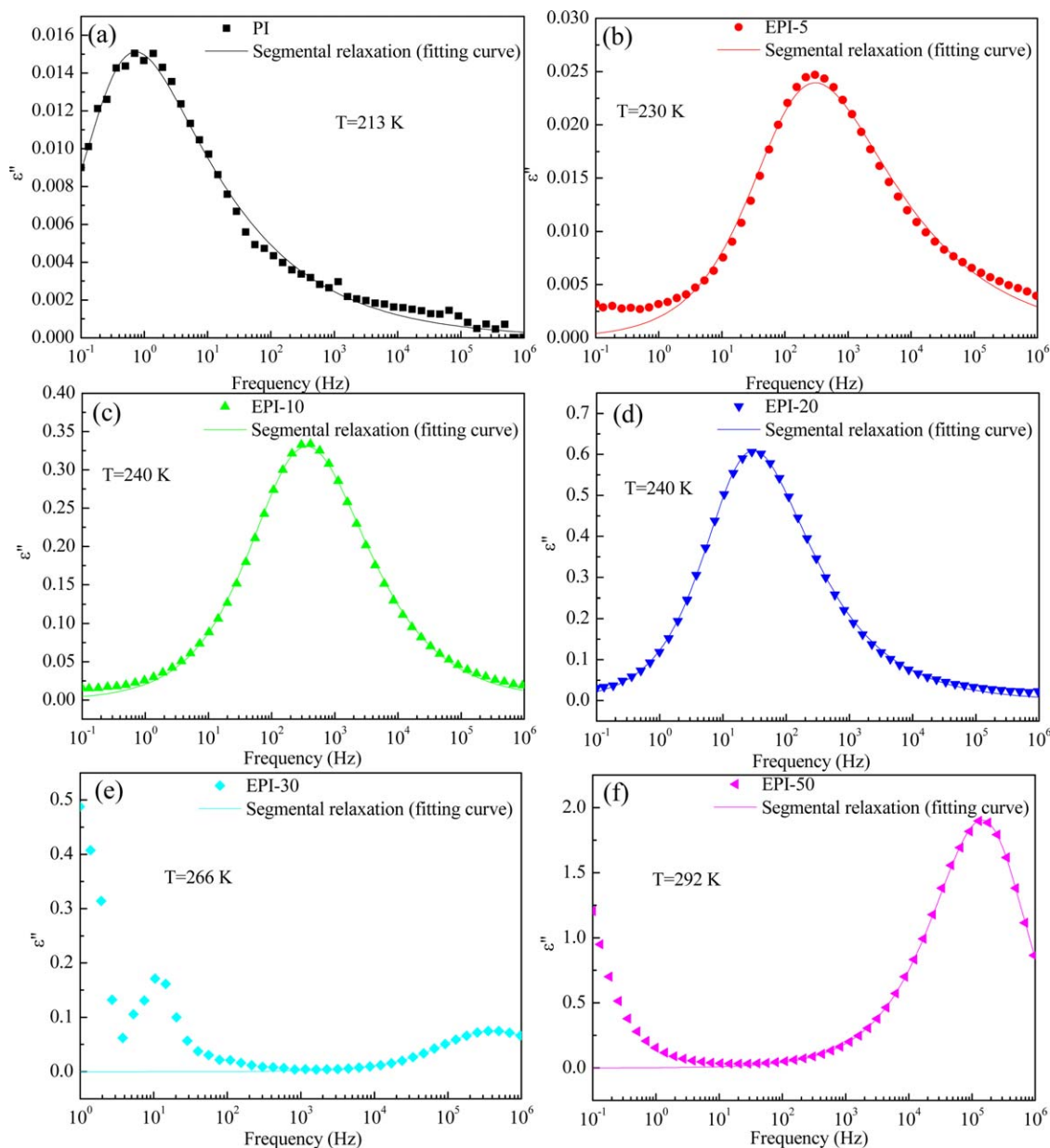


Figure 6. Dielectric loss of PI and EPI as a function of frequency. (a) PI, (b) EPI-5, (c) EPI-10, (d) EPI-20, (e) EPI-30, and (f) EPI-50. Solid lines represent the HN fitting curves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. HN Parameters for Segmental Relaxation of PI

Temperature (K)	$\Delta\epsilon$	τ_{HN} (s)	τ_{max} (s)
213	6.5790×10^{-2}	5.0520×10^{-1}	2.0010×10^{-1}
218	6.6467×10^{-2}	1.4891×10^{-2}	1.0720×10^{-2}
223	6.3035×10^{-2}	1.8256×10^{-3}	1.0770×10^{-3}
228	5.8953×10^{-2}	2.1271×10^{-4}	1.4820×10^{-4}
233	5.7308×10^{-2}	2.5794×10^{-5}	2.5790×10^{-5}
238	5.4570×10^{-2}	6.7980×10^{-6}	6.7980×10^{-6}
243	4.5614×10^{-2}	2.2317×10^{-6}	2.2320×10^{-6}
248	3.7400×10^{-2}	1.0920×10^{-6}	1.0920×10^{-6}

Table IV. HN Parameters for Segmental Relaxation of EPI-5

Temperature (K)	$\Delta\epsilon$	τ_{HN} (s)	τ_{max} (s)
220	1.1685×10^{-1}	8.0545×10^{-2}	2.808×10^{-2}
230	1.0658×10^{-1}	1.2904×10^{-3}	5.378×10^{-4}
240	9.8950×10^{-2}	6.3060×10^{-5}	3.034×10^{-5}
250	9.3727×10^{-2}	7.5058×10^{-6}	3.506×10^{-6}
260	8.0180×10^{-2}	8.2730×10^{-7}	5.945×10^{-7}
270	6.6284×10^{-2}	1.5900×10^{-7}	1.590×10^{-7}

$$\tau^* = [(1-n)\omega_c^n \tau_0]^{1/(1-n)} \quad (3)$$

where $\beta = 1 - n$.¹⁷ The value of n usually depends on molecular structure. Insight into the relationship between parameter n and molecular structure requires interpretation of the physical significance of the parameter n . The value of $n = 0$ connotes exponential relaxation (Debye relaxation). This coupling parameter n indicates the strength of the intermolecular interaction, thus provides a measure of the degree of cooperativity associated with the relaxation process, as shown in Table II. For segmental relaxation, intermolecular interaction between segments densely packed together in bulk polymer are responsible for the rate slowing down. The increase of parameter n indicates that epoxidation modification enhances the cooperativity of the segmental relaxation process. Also, epoxidation modification makes molecular chains need larger free volume during conformational transition, as presented in Figure 1. As a consequence, the mutual encounter of molecular chains becomes more probable with the

increase of the epoxidation degrees. It is reasonable to conclude that the oxirane groups as steric interference enhance the cooperativity of segmental relaxation process, retard the relaxation and increase the breadth of the dielectric dispersion.^{25,32}

Segmental Relaxation Motion

The analysis of the dielectric spectra is made by using empirical equation of Havriliak and Negami (HN).³⁷ In this model, the frequency dependences of the dielectric complex (ϵ^*) can be described by³⁸

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{[1 + (i\omega\tau_{HN})^\alpha]^\beta} \quad (4)$$

where $\Delta\epsilon = \epsilon_s - \epsilon_\infty$ is the dielectric strength, ϵ_s and ϵ_∞ are the relaxed and unrelaxed values of dielectric constant, the parameters α and β ($0 < \alpha, \alpha\beta \leq 1$) define the symmetrical and asymmetrical broadening of the loss peak, and τ_{HN} is the characteristic relaxation time. The segmental relaxation of PI

Table V. HN Parameters for Segmental Relaxation of EPI-10

Temperature (K)	$\Delta\epsilon$	τ_{HN} (s)	τ_{max} (s)
230	1.334	2.450×10^{-2}	1.899×10^{-2}
240	1.248	5.905×10^{-4}	4.372×10^{-4}
250	1.175	3.913×10^{-5}	2.827×10^{-5}
260	1.099	4.558×10^{-6}	3.398×10^{-6}
270	1.013	7.881×10^{-7}	6.348×10^{-7}
280	8.794×10^{-1}	1.705×10^{-7}	1.705×10^{-7}
290	8.201×10^{-1}	9.749×10^{-8}	4.065×10^{-8}
300	8.088×10^{-1}	1.650×10^{-8}	1.622×10^{-8}

Table VI. HN Parameters for Segmental Relaxation of EPI-20

Temperature (K)	$\Delta\epsilon$	τ_{HN} (s)	τ_{max} (s)
230	2.328	1.225	7.593×10^{-1}
240	2.146	8.836×10^{-3}	5.139×10^{-3}
250	2.029	2.784×10^{-4}	1.661×10^{-4}
260	1.942	2.246×10^{-5}	1.338×10^{-5}
270	1.861	3.238×10^{-6}	1.926×10^{-6}
280	1.717	4.820×10^{-7}	3.786×10^{-7}
290	1.548	1.555×10^{-7}	1.201×10^{-7}
300	1.423	3.742×10^{-8}	3.742×10^{-8}

and EPI can be excellent fitted using HN equation, as shown in Figure 6.

The relation between τ_{HN} and τ_{max} is given by³⁹

$$\tau_{max} = \tau_{HN} \left[\sin \frac{\pi\alpha\beta}{2(1+\beta)} \right]^{\frac{1}{\alpha}} \left[\sin \frac{\pi\alpha}{2(1+\beta)} \right]^{-\frac{1}{\alpha}}; f_{max} = \frac{1}{2\pi\tau_{max}} \quad (5)$$

where f_{max} is the frequency at which ϵ'' passes through the maximum value. The HN fitting parameters indicate the most important feature of polymer that being cooled to the glass transition region, samples exhibit the increased τ , as shown from Tables III–VIII. Such slow dynamics are because of segmental motion hindered by cooling temperature. For conventional glass forming materials, a slight decrease of $\Delta\epsilon$ with temperature is characteristic, reflecting the decreasing cooperativity of the observed dynamic process at higher temperature. This is also observed in Figure 7(a) which shows temperature dependence of $\Delta\epsilon$ for segmental motion. Also, Figure 7(a) presents the increased $\Delta\epsilon$ of segmental motion with increasing modification degree in the vicinity of their T_g . Such observations can be explained by the increased number of the effective dipole moment of system at higher modification degree. Furthermore, the fitting parameter α value trend in Figure 7(b) demonstrates the increasing cooperativity of segmental motion with increasing epoxidation degree, which is agreement with Figure 5(b).

Table VII. HN Parameters for Segmental Relaxation of EPI-30

Temperature (K)	$\Delta\epsilon$	τ_{HN} (s)	τ_{max} (s)
256	3.212	3.504×10^{-4}	2.703×10^{-4}
266	2.797	2.591×10^{-5}	1.563×10^{-5}
276	2.750	5.994×10^{-6}	2.549×10^{-6}
286	2.622	7.826×10^{-7}	4.007×10^{-7}
296	2.629	2.774×10^{-7}	1.025×10^{-7}
306	2.557	3.260×10^{-8}	3.260×10^{-8}

Table VIII. HN Parameters for Segmental Relaxation of EPI-50

Temperature (K)	$\Delta\epsilon$	τ_{HN} (s)	τ_{max} (s)
262	5.674	1.100×10^{-2}	5.985×10^{-3}
272	5.636	5.880×10^{-4}	1.008×10^{-4}
282	5.079	1.858×10^{-5}	1.446×10^{-6}
292	4.855	1.266×10^{-6}	1.266×10^{-6}
302	3.854	8.840×10^{-7}	8.840×10^{-7}

The above mentioned analyzes that the increased breadth of the dielectric dispersion for EPI primarily reflects that the enhanced intermolecular action can also be corroborated by the temperature dependence of the segmental relaxation time. It is well established that the temperature dependence of τ can be well described by Vogel-Fulcher-Tammann (VFT) equation, which is given by^{40–42}

$$\tau_{max} = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \quad (6)$$

where τ_0 and B are empirical parameters and T_0 is the so-called Vogel temperature, as exhibited in Table IX. The τ_{max} plotted as a function of inverse temperature for the all samples is shown in Figure 8. It is obvious that the curve slope absolute value of PI is higher than that of EPI, as the temperature increases. Such phenomenon indicates that in the vicinity of

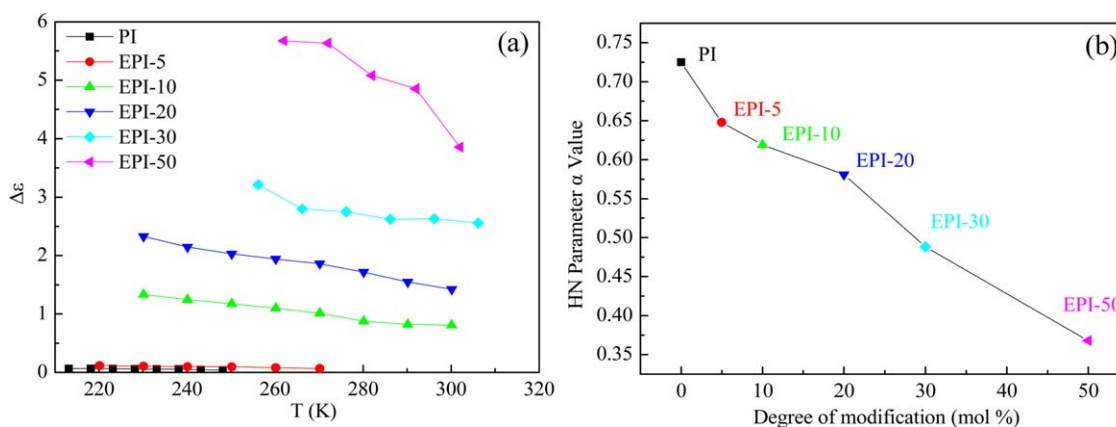


Figure 7. Fitting parameters for PI and EPI. (a) Temperature dependence of dielectric strength for segmental motion. (b) The parameter α value as a function of modification degrees in the vicinity of their glass transition region. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

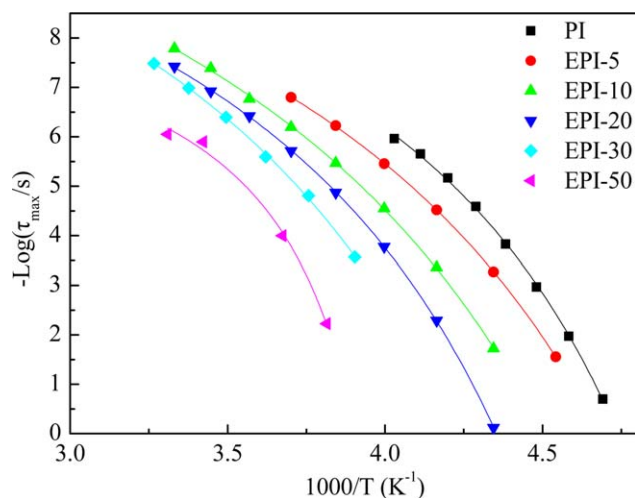


Figure 8. Temperature dependences of the characteristic relaxation time of PI and EPI. Solid lines represent the VFT fitting curves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

T_g the temperature dependence of τ of PI is stronger than that of EPI. As mentioned in the introduction, the segmental relaxation is a cooperative process which can be characterized by ξ .¹⁵ Based on this view, we suppose that the faster increase of τ with decreasing temperature can be explained by the stronger temperature dependence of ξ which goes to infinity as temperature approaches T_0 . According to the previous literature,²⁷ this ξ is proportional to $1/(T-T_0)^{2/3}$ with $\xi(T_g) \approx 2-3$ nm for polymers. In addition, the change of ξ is responsible for the change of friction coefficient and the increase of intermolecular interaction results from the change of ξ . It is evident that PI with higher epoxidation degree exhibits the longer relaxation time in Figure 8. These facts indicate that the segmental relaxation with higher epoxidation degree shows much more cooperative process and near the T_g segmental relaxation of all samples cannot be described by the same friction coefficient. Obviously, EPI exhibits longer ξ than PI from Figure 8. The longer ξ indicates the increased intermolecular interaction between segments which is in agreement with dielectric relaxation behavior and DSC analysis. Meanwhile, it makes temperature sensitivity of segmental motion decrease. Therefore, it is reasonable to conclude that PI exhibits the stronger temperature dependence of ξ , compared with the temperature dependence of ξ for EPI.

Table IX. The VFT parameters for PI and EPI

Sample	τ_0 (s)	B	T_0 (K)
PI	1.566×10^{-7}	793.8	156.8
EPI-5	2.217×10^{-6}	685.1	169.4
EPI-10	4.204×10^{-6}	574.0	167.1
EPI-20	4.979×10^{-6}	558.8	183.9
EPI-30	2.103×10^{-5}	476.6	184.5
EPI-50	1.860×10^{-4}	355.6	237.8

CONCLUSIONS

In summary, we have made an experimental study of the influence of epoxidation on segmental relaxation of PI. With the increase of epoxidation degree, T_g increases. The epoxidation modification increases the breadth of dielectric dispersion. Because segmental motion is the result of cooperative motion of repeat unit, the increase of breadth originates from interaction among cooperative motion. The increase of parameter n from coupling model clearly indicates that epoxidation enhances intermolecular interaction among cooperative motion. To further illustrate the above analysis, VFT is used to associate relaxation time with temperature. In VFT analysis, it is clearly seen that epoxidation retards relaxation time and the temperature dependence of segmental motion of PI is much stronger than that of EPI. This is because of the stronger temperature dependence of ξ of PI, compared with that of EPI.

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