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Evaluation on the degrading behavior of melt polyolefin elastomer with dicumyl peroxide in oscillatory shear flow by Fourier transform rheology

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Abstract

The degradation of melt polyolefin elastomer (POE) at the presence of dicumyl peroxides (DCP) was estimated at elevated temperature in oscillatory shear flow. Large amplitude oscillatory shear (LAOS) experiments followed by Fourier transform rheology (FTR) were carried out to detect and evaluate the branching architecture of the products. The third complex harmonic (I_3*) and other two parameters, small strain elastic shear modulus (M) and large strain elastic shear modulus (L), which describe the nonlinearity and elasticity of a material obtained from FTR, are mainly used to characterize the topological structure of polymer chains. The results indicate the degradation appeared just after a large amount of the long chain branches (LCB) created rather than as soon as the reaction started when the strain was applied within the linear viscoelastic regime of the original POE at high frequencies. This is different from our previous result that the dominant reaction was coupling in linear shear flow. The threshold strain for degradation decreased with the oscillatory frequency, and the frequency owned a different acting mechanism from the strain amplitude to cause the degradation reaction. Moreover, there is a kind of selectivity of shear rate on the polymer chains for degradation. Low frequency results in short linear scission segments and a long branched chain suffers from degradation more than once. At high frequency, the possibility of degradation at the sites near the branching points of LCB increases.

Keywords: POE; Oscillatory shear flow; Degradation

1. Introduction

In our previous paper [1], the effect of shear flow on the reaction of polyolefin elastomer (POE) at the presence of peroxides at elevated temperature has been investigated. Both coupling and degrading reactions were observed. Although it is general known that the degradation occurs in the manner of β-scission, it also includes another counter course, referred to as a recombination reaction of the secondary macromolecular radical (C_R) and the polymer chain with a double bond ($C_=$) produced by β-scission. The main reaction mechanism is shown in Scheme 1 and we labeled the structure of isolated tertiary carbon with "br1" and the structure of two tertiary carbons in a chain separated by only one CH_2 group with "br2". Actually, the chain scission is possible just when the tertiary carbon radical is in the form of br2, which has been confirmed by ^{13}C NMR spectroscopy [1]. β-scission is a kind of monomolecular reaction and should be attributed to the chemical and structural properties of the reactant and independent of the shear flow field. It is even believed that β-scission could also occur in quiescent state. But the counter reaction (recombination) which is diffusion controlled can be affected by the shear flow field greatly in such entanglement system [2,3]. The key factor for the recombination is the relative distance between the active sites of C_R and $C_=$. In fact, the degradation indeed occurs just when the recombination is not dominant, so the probability of degradation of POE depends on the shear flow field imposed upon the reaction system. In

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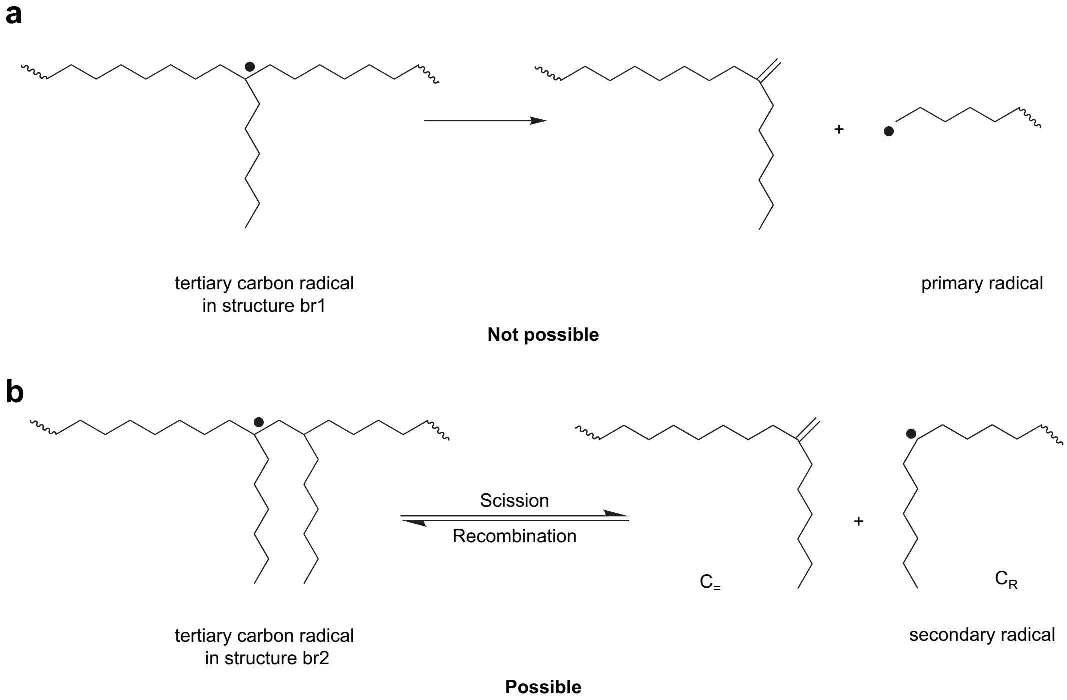


Scheme 1. Scission reactions of tertiary carbon radicals in structure br1 (a) and br2 (b).

POE/peroxide system, the coupling reaction is dominant in linear shear flow which is same as the case of polyethylene with peroxides, whereas the POE chain is also able to degrade when the strain rate exceeds the linear regime. Moreover, we found that the critical strain amplitude for the degradation of POE in oscillatory shear flow altered with the applied oscillatory frequency [1]. The applied strain amplitude and frequency seem to influence the distance between C_R and $C_=$ in different ways. So it is necessary to make clear the action mechanism of frequency and strain amplitude, including whether they have different effects on the degrading behavior of POE chains and how they act, respectively.

Usually in the system of commercial polyolefin modified by peroxides, the long chain branches (LCB) are always created by coupling reaction whereas the degradation can tailor the length of polymer chains. There are few changes in functional groups, but the molecular weight and its distribution as well as topological structures of polymer chains change a great deal. Since the polymer architecture is so crucial as to influence the reaction process and the property of final product, it is very important to understand it clearly and control it. In the usual testing methods, gel permeation chromatography (GPC) can directly give the molecular weight distribution of product but without the information of topological structure of polymer chains. The use of ^{13}C NMR is also limited because it is unable to differentiate between branches with six or more carbon atoms. However, the rheology is one suitable tool owning the advantage for determination of macromolecular structure. Due to the more complicated topological structure of LCB, the characterization is more difficult than that of the linear chain. Compared with many rheological methods such as small amplitude oscillatory shear (SAOS), vGP plot, Cole–Cole plot and stress relaxation, Fourier transform rheology (FTR) generally following the large amplitude oscillatory shear (LAOS) experiments is one more powerful rheological methodology to estimate LCB. The continuous application of LAOS is a simple way to actualize the nonlinear condition and has been proved very sensitive to the microstructure of the fluids, e.g., by Giacomine and Dealy [4], Hyun et al. [5,6]. Even though the validity of linear viscoelasticity fails with large strain amplitude, more information can be obtained through the analysis of the response in the Fourier space. The approach of FTR has already been presented by Wilhelm et al. [7–10] and Neidhöfer et al. [11,12] on the linear polymer melts and solutions and branched polymers. Fleury et al. [13], Schlatter et al. [14] and Vittorias et al. [15] have also applied this technique on the linear and branched industrial polyethylenes, the relative intensities (I_n/I_1) and phase shifts (Φ_3) of the higher harmonics between them in the frequency spectrum were distinguishing extremely. In a similar way, we can study the molecular architectures of the reaction products containing linear and branched polymers and speculate on how they are formed under shear flow field.

The purpose of this paper is to investigate how the critical strain amplitude for the degradation varies with the frequency and give the action mechanism of both the applied strain amplitude and frequency on such degrading behavior of POE chains in oscillatory shear flow. For this purpose, we have utilized LAOS followed by FTR to characterize the products created in different conditions of oscillatory shear flow. According to the analysis of rheological measurements and FTR, we could try to confirm where is the site for the effective β-scission on the polymer chain.

2. Experimental

2.1. Materials

The experimental polymer used in this study is poly(ethylene-*co*-α-butene) (PEB). It was produced by copolymerization of ethylene with α-butene via a single-site metallocene catalyst technique resulting in the ethyl short branches. PEB grade Tafmer A-4085, with the butene content of 13.3 mol% (determined from ^{1}H NMR analysis), melt flow index of 3.6 g/10 min (190 °C, 2.16 kg), and density of 0.885 g/cm^3 (20 °C), was obtained from Mitsui Chemicals, Japan. Its number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) are 55.4 kg/mol and 2.3, respectively. Dicumyl peroxides (DCP, analytically pure), purchased from Shanghai Chemicals Factory, PR China, were used without any further treatment. The decomposition rate constant of DCP, k_d, is $9.233 \times 10^{-7}\ \mathrm{s}^{-1}$ at 90 °C and $3.40 \times 10^{-3}\ \mathrm{s}^{-1}$ at 160 °C, as provided by the suppler, and the half-life time is 208.5 h and 204 s at 90 °C and 160 °C, correspondingly.

2.2. Sample preparation and rheological measurement

The pellets of PEB (40 g) were impregnated with an acetone solution of DCP (0.15 g) over 12 h at room temperature, which was followed by evaporation at a low pressure to remove the residual solvent. Then the PEB sample with DCP concentration of 0.0139 mol/kg was premixed in a torque rheometer (Haake Rheocord90, Germany) at 90 °C with the rotor speed 60 rpm and taken out after 6 min to compress into sheet (thickness ≈ 1 mm) at the same temperature under 12 MPa. Even though the half-time of DCP at 90 °C is as long as 208.5 h, it is still possible to have a small amount of reaction during the preparation. However, this will not affect our experimental results very much, and can be paid little attention to reasonably. It is also believed that the mixing in torque rheometer makes the peroxides dispersed homogeneously in the matrix of PEB. This means there is no spatial gradient of peroxide, which makes the diffusion of DCP less important. This is different from those experiments where inhomogeneous state of peroxide makes the diffusion of peroxide crucial for reactions [16].

Our rheological tests were all performed on a rotating rheometer (Gemini 200HR, Bohlin Instruments, UK) with parallel plate geometry of 25 mm in diameter and a gap of 1 mm. First of all, the stability of original PEB sample was checked through the measurement of G' and G'' at 0.6283 rad s^{-1} in the linear viscoelastic regime. There is few changes of dynamical modulus on a large time scale (over 3 h) at 160 °C with a strain amplitude of 5% that illustrated the effect of the thermal oxidation can be excluded reasonably (Fig. 1). Before each rheological evaluation of reaction, the preparing period, including the time of heating, compressing the sample and stabilizing the temperature, was controlled as short as possible to minimize the reaction. The test temperature was hold at 160 °C for all rheological experiments.

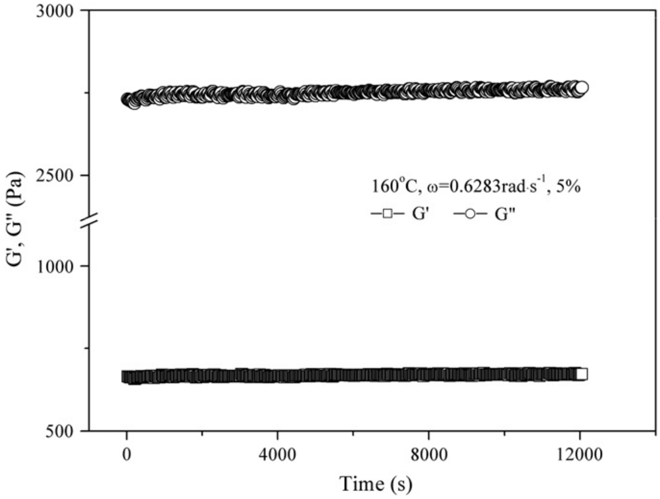


Fig. 1. Dynamic time sweeps of original PEB for 200 min ($\omega = 0.6283$ rad s^{-1}, strain amplitude = 5%, 160 °C).

The dynamic time sweeps to monitor the reacting processes were performed at 37.70 rad s^{-1} with the strain amplitudes of 1%, 10% and 25%, at 9.425 rad s^{-1} with the strain amplitudes of 14% and at 157.1 rad s^{-1} with the strain amplitudes of 14% for the same duration and the products were labeled with Pro001(37.70 rad s^{-1}), Pro010(37.70 rad s^{-1}), Pro025(37.70 rad s^{-1}), Pro014(9.425 rad s^{-1}) and Pro014(157.1 rad s^{-1}), respectively. The measurements of small amplitude oscillatory shear were carried out for all products, and the frequencies were in the range of 0.01–100 rad s^{-1} with a given strain amplitude of 1%. The strain amplitude sweeps were applied for the original and the fully coupled PEB at the same frequency. Afterwards the large amplitude oscillatory shear experiment was performed for each product at 0.6283 rad s^{-1}. The range of strain amplitude was from 25% to 450%, and the data of torque were recorded after the sample achieved the steady state with the certain strain amplitude, because the stable signal cannot be set up instantaneously due to the viscoelasticity of the matrix.

After rheological measurements, each reacted sample was cut into small pieces and extracted in a fabric bag with an excess volume of xylene employing Soxhlet extractor for 24 h at about 120 °C for further determination of gel content. Then the extracted fabric bags were dried in vacuum to a constant weight. The results revealed there were no gels in the modified PEB samples, so the phase separation induced by the creation of microgels can be avoided and homogeneous reaction system is kept for the whole reacting process.

3. Results and discussions

3.1. Rheological evaluation

The storage modulus (G') monitored here as a function of reaction time in the oscillatory shear flows with strain amplitudes of 1%, 10% and 25% at 37.70 rad s^{-1} is shown in Fig. 2. We marked the products with Pro001(37.70 rad s^{-1}),

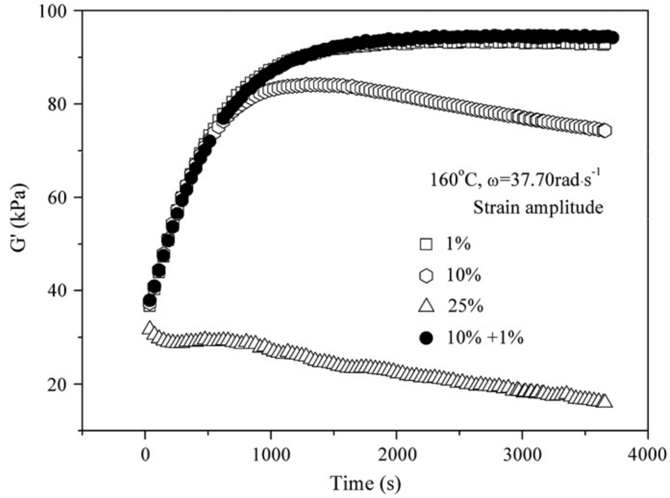


Fig. 2. Dynamic time sweeps with different applied strains ($\omega = 37.70$ rad s^{-1}, 160 °C). The (●) represents the reaction process was carried out with a strain amplitude of 10% for 512 s and then with a strain amplitude of 1% for the last period.

Pro010(37.70 rad s^{-1}) and Pro025(37.70 rad s^{-1}), respectively, and the number in each legend denoted the corresponding strain amplitude given in each test. For small strain amplitude (1%) in the linear regime, G' increased monotonously all the time and reached a final plateau. This should be a result of the coupling reactions of two macromolecular radicals leading to an increase in the degree of branching and overall increase in the molecular weight of the system. Correlating the SAOS of all products shown in Fig. 3, the complex viscosity of the product of Pro001(37.70 rad s^{-1}) was much higher than that of pure POE at low frequency, and tended to coincide at high frequency. Since there were no gels formed in the sample, the increased viscosity at low shear rate and enhanced shear thinning could be attributed to the formation of long chain branches in the sample [17]. In the case with the strain amplitude of 25%, G' decreased with the time in the whole process (Fig. 2). This behavior is attributed to two possible reasons. Firstly, the large strain amplitude was applied in this experiment. Strain amplitude (25%) doesn't lie in the linear regime for pure POE (Fig. 4), which could possibly decrease the value of G' with time due to the disentanglements of polymer chains in such nonlinear shear flow. Secondly, it is possible that the molecular weight of the system decreased which was probably caused by the degradation reaction. From the frequency dependence of oscillatory complex viscosity η^* for the product of Pro025(37.70 rad s^{-1}) in Fig. 3, two points could be observed. Firstly, the shear thinning was enhanced and η^* of this product was higher than that of pure POE at low frequency. This should be induced by the creation of new topological structure (such as long chain branch) through the coupling reaction, even though it was not displayed in the curve of time sweep. Secondly, the overall η^* of this product was much lower than the one of Pro001(37.70 rad s^{-1}). This confirmed that the decrease in the molecular weight really happened under the oscillatory shear with larger strain amplitude. So it is the nonlinear shear flow that induces the degradation in our reaction system, which is consistent with our previous results [1].

However, it was not very sure whether the degradation occurred in the case with the strain amplitude of 10%, which shows an increase of G' followed by a decrease of G' at long time shear. The decrease in the storage modulus might be ascribed to the degradation as well as the change of linear regime for the sample during the experiment. Strain amplitude (10%) lies in the linear regime at the beginning of the reaction and should go into the nonlinear regime due to the creation of LCB as the reaction proceeded (Table 1). This could possibly decrease the value of G' with time. On the other hand, the overall η^* of Pro010(37.70 rad s^{-1}) in Fig. 3 was not obviously lower than those of Pro001(37.70 rad s^{-1}) gained in the test with small strain amplitude. So the validity of above rheological methodologies fails and the entire analysis of this experiment cannot be fulfilled. In order to distinguish whether the degradation occurred in this case, we carried out the LAOS experiments followed by the analysis of FTR.

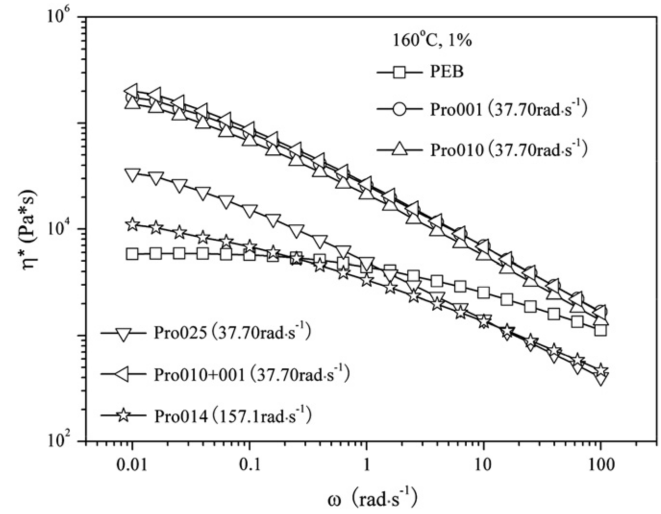


Fig. 3. Small amplitude mechanical spectrometry of the original PEB and all products (strain amplitude = 5%, 160 °C).

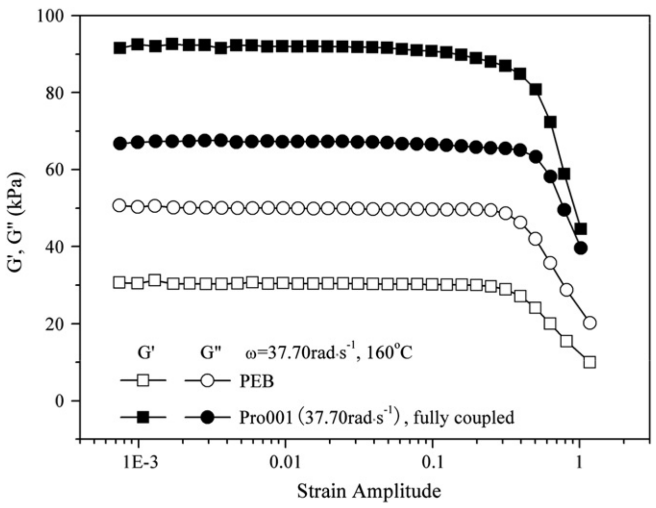


Fig. 4. Dynamic strain sweeps of original and fully coupled PEBs ($\omega = 37.70$ rad s^{-1}, 160 °C).

Table 1
Critical conditions for degradation of PEB at different frequencies in oscillatory shear flow

ω (rad s^{-1})	Linear regime for original PEB	Linear regime for coupled PEB	Critical strain γ_0 (%)	Critical shear rate $\dot{\gamma}_{\max}$ (s^{-1})	Q_n ($n = 1, 2$)
0.6283	$\gamma \leq 24.6\%$	$\gamma \leq 19.7\%$	25	0.157	1.1×10^2
2.513	$\gamma \leq 24.6\%$	$\gamma \leq 16.9\%$	25	0.628	5.1×10^1
9.425	$\gamma \leq 23.6\%$	$\gamma \leq 7.0\%$	14	1.319	7.0×10^3
37.70	$\gamma \leq 15.7\%$	$\gamma \leq 3.9\%$	8	3.016	1.6×10^4
157.1	$\gamma \leq 9.9\%$	$\gamma \leq 3.9\%$	2	3.142	1.0×10^6

3.2. LAOS and FTR

The typical stress curve with large strain amplitude is shown in Fig. 5. Although the stress response keeps the periodicity, it cannot be represented by a single harmonic function. The nonlinear effects displayed as the deformations of the harmonic signal, such as the squeeze near the peaks and valleys and a dissymmetry compared to the vertical line crossing the maximum value. However, after discrete Fourier transformation the frequency spectrum of the stress intensity was obtained, in which the nonlinear effects were much clearer (Fig. 6). The third complex harmonic of stress (σ_3^*) is here paid more attention to, and can be expressed as:

$$\sigma_3^* = \sigma_3\left(\cos\ \varphi_3 + i\ \sin\ \varphi_3\right) \tag{1}$$

where σ_3 and φ_3 denote the magnitude and phase of the third complex harmonic of stress, respectively. Correspondingly, σ_1 and φ_1 represent the magnitude and phase of the fundamental σ_1^*. Then the relative intensity of stress (σ_3/σ_1) and the phase shift (Φ_3) can be chosen as parameters to characterize the nonlinear effect in the periodic stress curve [14]. Φ_3 is defined as:

$$\Phi_3 = \varphi_3 - 3\varphi_1 \tag{2}$$

Similarly, the storage modulus (G_3') and loss modulus (G_3'') can be written as:

$$G_3' = \frac{\sigma_3}{\gamma_0}\cos\ \varphi_3 \tag{3}$$

$$G_3'' = \frac{\sigma_3}{\gamma_0}\sin\ \varphi_3 \tag{4}$$

where γ_0 stands for the strain amplitude.

The relative stress intensities (σ_3/σ_1) for all products and original PEB are shown in Fig. 7. Notably, all the products exhibit evident nonlinearities compared with the original PEB. This kind of nonlinearity should come from the creations of LCB. This result proves the existence of coupling reaction in the case with the strain amplitude of 25% at 37.70 rad s^{-1} again. According to this figure, two more points can be obtained. Firstly, the nonlinearity of Pro001(37.70 rad s^{-1}) is much stronger than those of Pro010(37.70 rad s^{-1}) and Pro025(37.70 rad s^{-1}), especially under larger strain amplitudes. Due to the same concentration of peroxides in each sample, the amount of LCB is probably not very different. So the weaker nonlinearities of Pro010(37.70 rad s^{-1}) and Pro025(37.70 rad s^{-1}) should be attributed to the different topological structures of the LCB. It can be inferred that the arm lengths of LCB in Pro010(37.70 rad s^{-1}) and Pro025(37.70 rad s^{-1}) are statistically shorter than those in the fully coupled sample, which should be induced by the degrading behavior acting on the LCB. At this rate, the judgment that the degradation occurred in the case with the strain amplitude of 10% at 37.70 rad s^{-1} can be made. Secondly, the nonlinearity of Pro010(37.70 rad s^{-1}) is stronger than that of Pro025(37.70 rad s^{-1}), which indicates that the degree of branching of Pro025(37.70 rad s^{-1}) is lower than that of

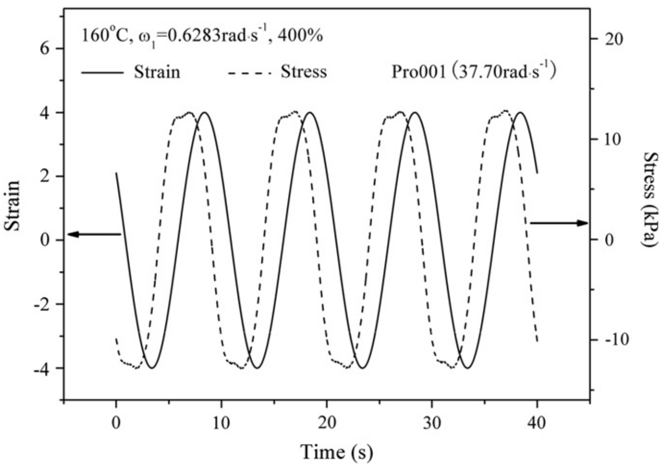


Fig. 5. Profiles of strain and stress for Pro001(37.70 rad s^{-1}) (fundamental frequency $\omega_1 = 0.6283$ rad s^{-1}, strain amplitude = 400%, 160 °C).

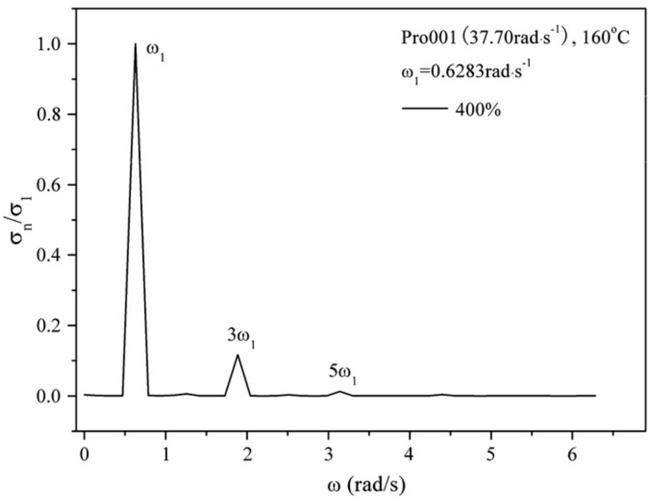


Fig. 6. Normalized frequency spectrum of the stress intensity (fundamental frequency $\omega_1 = 0.6283$ rad s^{-1}, strain amplitude = 400%, 160 °C).

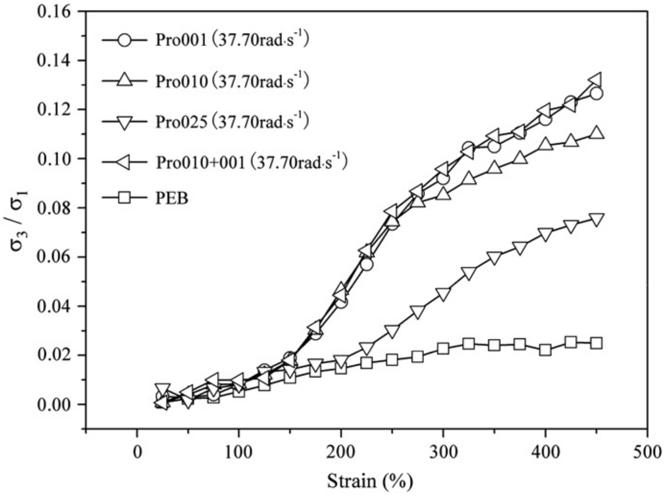


Fig. 7. The relative stress intensity (σ_3/σ_1) for original PEB and all products with the strain amplitude from 25% to 450% (fundamental frequency $\omega_1 = 0.6283$ rad s^{-1}, 160 °C).

Pro010(37.70 rad s^{-1}). So the larger the applied strain amplitude is, the seriously the sample degrades at the same oscillatory frequency.

The similar trends and results can also be found in the plots of Φ_3 (Fig. 8). Meanwhile, the Cole–Cole plot of the third complex harmonic is shown in Fig. 9. The nonlinearity increases with the radius of the half loop, so it is easier to judge whether the sample has suffered from the degradation and how seriously it degraded following the same way. On the other hand, there are two parameters for quantifying nonlinear elastic response in large amplitude oscillatory shear [18]: small strain elastic shear modulus (M) and large strain elastic shear modulus (L), which are defined as followed and shown in Fig. 10:

$$M(\omega, \gamma_0) = \left.\frac{\mathrm{d}\sigma}{\mathrm{d}\gamma}\right|_{\gamma=0} = \sum_{\substack{n=1 \\ n \text{ odd}}}^{N} nG'_n(\omega, \gamma_0) \tag{5}$$

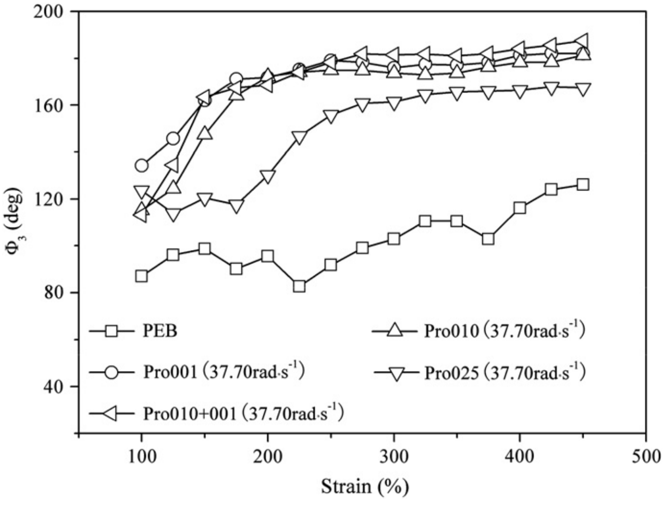


Fig. 8. The phase shift (Φ_3) for original PEB and all products with the strain amplitude from 25% to 450% (fundamental frequency $\omega_1 = 0.6283$ rad s^{-1}, 160 °C).

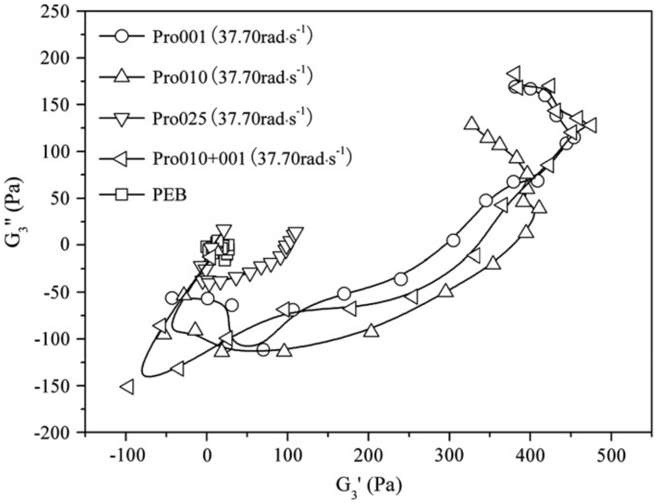


Fig. 9. The Cole–Cole plot ($G_3'' \sim G_3'$) at the third frequency for original PEB and all products with the strain amplitude from 25% to 450% (fundamental frequency $\omega_1 = 0.6283$ rad s^{-1}, 160 °C).

$$L = \frac{\sigma|_{\gamma=\pm\gamma_0}}{\pm\gamma_0} = \sum_{\substack{n=1 \\ n \text{ odd}}}^{N} G'_n(\omega, \gamma_0) \tag{6}$$

It is then apparent that M and L reduce to G_1 in the linear regime, that is

$$\lim_{\gamma_0 \to 0} M(\omega) = \lim_{\gamma_0 \to 0} L(\omega) = G_1(\omega) \tag{7}$$

where G_1 represents the storage modulus at the fundamental frequency. Since the elastic response is sensitive to LCB, M and L are appropriate for evaluating the LCB.

According to the value of M and L for all products and original PEB is shown in Figs. 11 and 12, Pro010(37.70 rad s^{-1}) and Pro025(37.70 rad s^{-1}) exhibit the weaker nonlinear elastic responses compared with the fully coupled sample of Pro001(37.70 rad s^{-1}). And also we can obtain the same conclusions as the above mentioned. Different from the cases of

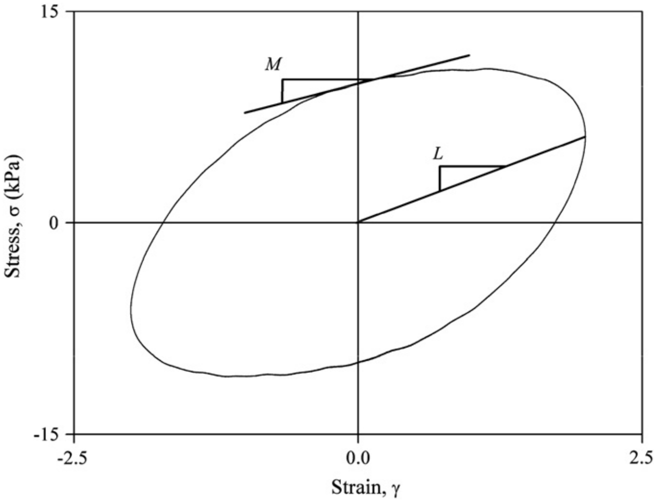


Fig. 10. Definitions of the small strain elastic shear modulus (M) and the large strain elastic shear modulus (L).

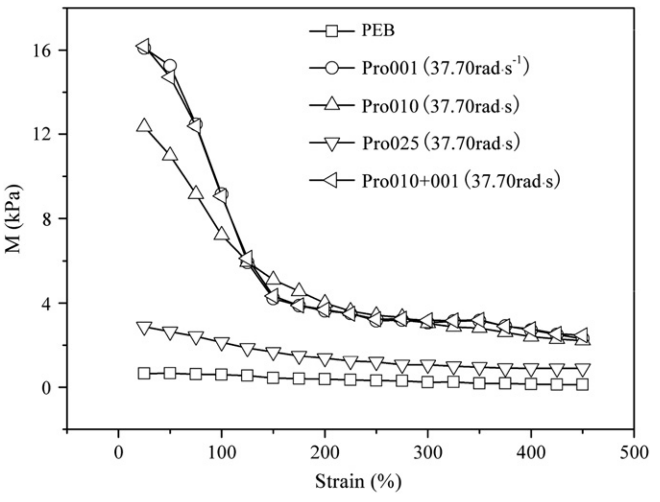


Fig. 11. The small strain elastic shear modulus (M) for original PEB and all products with the strain amplitude from 25% to 450% (fundamental frequency $\omega_1 = 0.6283\ \mathrm{rad\ s^{-1}}$, 160 °C).

the relative stress intensity, phase shift and the modulus of the complex third harmonic, notable differences in the nonlinearities of all products display mainly in the range of the low strain amplitudes. This feature can just compensate the drawbacks in the above methods. So we can correlate M and L with σ_3/σ_1, Φ_3, G_3' and G_3'' to make a more comprehensive estimation about the nonlinearity over the entire range of the applied strain amplitudes.

Since it is confirmed that the degradation indeed occurred in the case with the strain amplitude of 10% by FTR, we do some further studies on when the degradation started in this case. So a two-stage test was designed and carried out with 10% strain amplitude for the former 512 s and 1% strain amplitude for the last duration. Similarly, the product was labeled with Pro010 + 001(37.70 rad s^{-1}) and the results were displayed in the corresponding figures. As shown in Figs. 2 and 4, the whole reaction curve is nearly the same as the one with the strain amplitude of 1% and the overall η^* of Pro010 + 001 (37.70 rad s^{-1}) is similar to the one of Pro001(37.70 rad s^{-1}). Pro010 + 001(37.70 rad s^{-1}) also exhibits nearly identical nonlinearities referred to the Pro001(37.70 rad s^{-1}) over the entire range of studied strain amplitude by FTR (Figs. 7–9, 11 and 12). All these results reveal that the amount and topological structure of LCB in Pro010 + 001(37.70 rad s^{-1}) resemble those in Pro001(37.70 rad s^{-1}). Furthermore, it is indicated that there was no degradation for the former 512 s (10% strain amplitude) in this two-stage test. That is to say, in the case with the constant strain amplitude of 10% the degradation did occur and appeared just after a large amount of LCB had been created rather than as soon as the reaction started. Thus, it is can be concluded the degradation should start on the LCB, not on the linear chains.

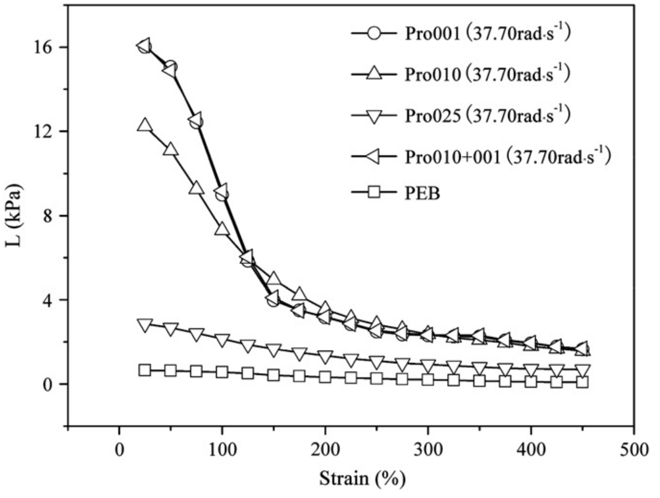


Fig. 12. The large strain elastic shear modulus (L) for original PEB and all products with the strain amplitude from 25% to 450% (fundamental frequency $\omega_1 = 0.6283\ \mathrm{rad\ s^{-1}}$, 160 °C).

3.3. *Effect of oscillatory frequency and proposed mechanism*

The critical strains for degradation of PEB at other several frequencies are listed in Table 1. The phenomenon that the degradation occurred even with the strains applied within the linear viscoelastic regime of original PEB arose when the frequency increased to 9.425 rad s^{-1}. The threshold strain for degradation decreased with the oscillatory frequency, whereas the maximum shear rate, $\dot{\gamma}_{\max}$, increased as the frequency grew and seemed to keep a fixed value when the frequency was not lower than 37.70 rad s^{-1}. This fact reveals that compared with the strain, the frequency owned a different action mechanism to cause the degradation reaction.

The main mechanism how the shear flow influenced the reaction of POE at the present of peroxides has been established, and the details in the cases at low frequencies have been also illuminated clearly [1]. We consider that β-scission could also occur even in quiescent state. But the counter reaction, referred to as a recombination reaction, can be affected by the shear flow field. We emphasized that the key factor for the degradation was the relative distance between the active sites of two parts created from β-scission. This distant at time t under the simple shear flow Γ can be expressed as:

$$\vec{\mathbf{x}}(t) = \exp(\Gamma\cdot t)\cdot\vec{\mathbf{x}}_0 + [\vec{\mathbf{x}}_D(t) - \vec{\mathbf{x}}_0] \tag{8}$$

where $\vec{x}_0$ is the original distant between the active sites of two parts created from β-scission, Γ is the strain rate, $\exp(\Gamma\cdot t)\vec{x}_0$ is the distant at time t if they moved only by advection and $\vec{x}_D(t)$ is the distant at time t if they moved only by diffusion and holds for $\vec{\mathbf{x}}_D(0) = \vec{\mathbf{x}}_0$. According to de Gennes [19], the relationship between the diffusive distance and time is as follows:

$$\Delta x_D^2(t) = (x_D(t) - x(0))^2 = 2D_{\mathrm{rep}}t \quad (t > t_{\mathrm{rep}}) \tag{9}$$

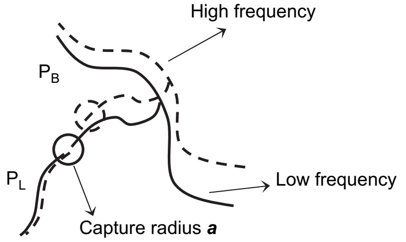
$$\text{or}\quad \Delta x_D^4(t) = (x_D(t) - x(0))^4 \cong \delta^2 D^{\mathrm{T}} t \quad (t_{\mathrm{R}} < t < t_{\mathrm{rep}}) \tag{10}$$

where δ is the diameter of the tube, D_{rep} and D^{T} are the corresponding diffusion coefficients, and t_{R} and t_{rep} are the Rouse time and repetition time of the corresponding polymer chain, respectively.

Although the degradation process is controlled by micro-diffusion and macro-convection, in oscillatory shear flow the relative distance still changes in a limited range. The strain determines the distance between the two-scission parts needed to diffuse for the recombination reaction, while the frequency determines the time allowing the two-scission parts to get together again. Since we are certain that the degradation did occur on LCB in the sample, the two-scission fractions should be a linear chain (P_L) and a LCB (P_B) displayed in Scheme 2. For a given strain amplitude within the linear viscoelastic regime of original PEB (example: the case with the strain amplitude of 10% at 37.70 rad s^{-1}), P_L can be still near the equilibrium position no matter at low or high frequency, due to the short relaxation time of linear chain. As for P_B, it can relax only at very low frequency, while at high frequency P_B can diffuse little distance due to the too long relaxation time and insufficient time to diffuse. This reasonably increases the relative distance between P_L and P_B, which is larger than the capture radius and in the order of some nanometers, and results in the effective scission. In such situation, it needs only small strain amplitudes to realize the degradation in oscillatory shear flow.

On the other hand, if the strain amplitude is fixed, for example, 2%, the degradation could occur just when the applied oscillatory frequency reaches or surpasses one certain value, for example, 157.1 rad s^{-1}. Since the material owns a homogeneous comonomer distribution, it can be reasonably considered that the site for scission is random on the PEB polymer chain and the length of linear scission fraction (P_L) should be also random. At low oscillatory frequency, both short and long P_L can relax due to the sufficient time, and the recombination rather than effective scission occurs. However, long P_L is not easy to relax due to the insufficient time at high oscillatory frequency, so the effective scission is ready to happen. It can be inferred that the higher the frequency is, the longer the P_L segment produced from scission is and more seriously the polymer chains degrade. Thus the probability of degradation at the sites approaching the branching points of LCB would increase. This means the molecular structures of scission fractions created at different oscillatory frequencies are not the same, and the shear flow field has the selectivity of degrading sites on the polymer chains.

In order to prove the above hypothesis, the reactions were also performed with the strain amplitude of 14% at both 9.425 rad s^{-1} and 157.1 rad s^{-1}, in which conditions of shear flow there's degradation during the reaction (Table 1). The products were named by Pro014(9.425 rad s^{-1}) and Pro014(157.1 rad s^{-1}), respectively. Figs. 13 and 14 display the relative stress intensities (σ_3/σ_1) and the large strain elastic shear modulus (L) for these two products. It is very clear that the degradation is more distinct at high frequency (157.1 rad s^{-1}) than at low frequency (9.425 rad s^{-1}) with the same strain amplitude of 14%. Particularly, the values of (σ_3/σ_1) and L for Pro014(157.1 rad s^{-1}) are very close to the ones for the original PEB in the experimental range of strain amplitude. This indicates that the LCB is few in Pro014(157.1 rad s^{-1}) and the topological structure of the polymer chains is mainly linear. Although the shear flow is strong enough for linear chains to possible degradation ($\dot{\gamma}_{\max} = 157.1 \times 0.14 \approx 22 \quad s^{-1}$), the LCB should be still created in the reacting process, which can



Scheme 2. Sketch of scission reactions of LCB: — at low frequency; --- at high frequency.

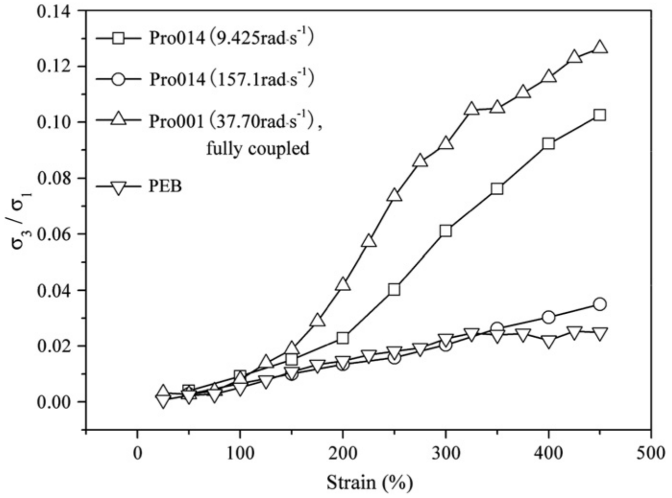


Fig. 13. The relative stress intensity (σ_3/σ_1) for original PEB and the products of Pro014(9.425 rad s^{-1}), Pro014(157.1 rad s^{-1}) and Pro001(37.70 rad s^{-1}) with the strain amplitude from 25% to 450% (fundamental frequency $\omega_1 = 0.6283$ rad s^{-1}, 160 °C).

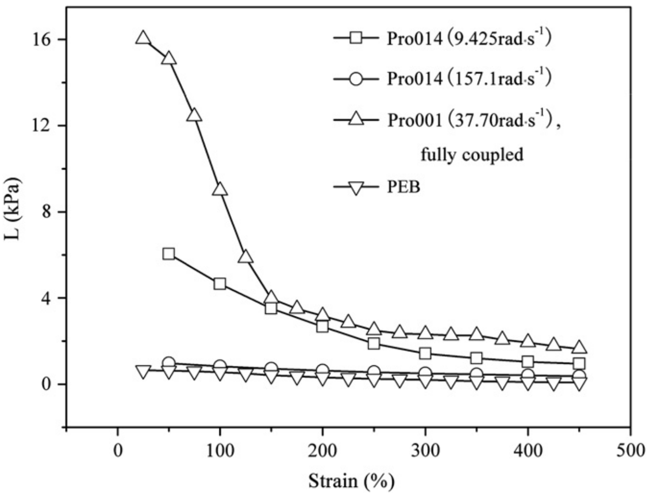


Fig. 14. The large strain elastic shear modulus (L) for original PEB and the products of Pro014(9.425 rad s^{-1}), Pro014(157.1 rad s^{-1}) and Pro001-(37.70 rad s^{-1}) with the strain amplitude from 25% to 450% (fundamental frequency $\omega_1 = 0.6283$ rad s^{-1}, 160 °C).

be judged by the small amplitude dynamic mechanical spectra of Pro014(157.1 rad s^{-1}) and original PEB is shown in Fig. 3. So it can be inferred a majority of the LCB change to linear chains again that is induced by the degradations at the sites approaching the branching points of LCB. This truly reflects the concept of the selectivity of the shear flow field on chains for the degradation, and the high shear rate increases the possibility of degradation at the sites approaching the branching points of LCB created by coupling reaction. The linear scission part, P$_L$, should be much longer than the one created at low frequency, for example, 9.425 rad s^{-1}.

Now we would like to give some quantitative estimation for the above discussion. If the two-scission parts, P$_L$ and P$_B$, were moved only by advection (Scheme 3), the relative distance between their active sites at time t should be:

$$x_\Gamma(t) = x(0)\cdot\sqrt{1+\gamma(t)^2} = x(0)\cdot\sqrt{1+A\cdot\gamma_0} \tag{11}$$

where A is a coefficient not bigger than unit, γ_0 stands for the strain amplitude and the time t depends on the frequency:

$$t \propto \frac{1}{f} \tag{12}$$

It is can be accepted that P$_B$ diffuses little, so at low frequency, such as 0.6283 rad s^{-1} and 2.513 rad s^{-1}, the diffusive distance of P$_L$ is:

$$\Delta x_D(t) = \sqrt{2D_{\text{rep}}t} \tag{13}$$

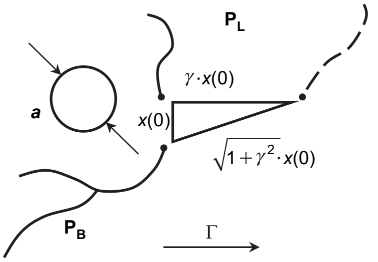
and D_{rep} is the coefficient of diffusion due to repetition, which can be expressed as:

$$D_{\text{rep}} = D_0\frac{N_e}{N_L^2} \tag{14}$$

where D_0 is a constant, N_L is the length of P$_L$ and N_e is the critical length of polymer chain higher than which entanglements become dominant.

In the critical condition of degradation, the relationship below can be obtained:

$$x_\Gamma(t) - \Delta x_D(t) = x(0)\sqrt{1+A\cdot\gamma_0} - \frac{1}{N_L}\sqrt{2D_0N_et} = a \tag{15}$$



Scheme 3. Sketch of distance between P_L and P_B if they moved only by advection.

The original distance which is not larger than the capture radius of a can be written as $x(0) = Ba$ (B is also a coefficient not bigger than unit), then

$$N_L^2 \propto f^{-1}\left(\sqrt{1+A\cdot\gamma_0} - B\right)^{-2} = Q_1^2 \tag{16}$$

In one extreme situation that $A = B = 1$, the values of Q_1 are listed in Table 1. So the length of P$_L$, which is created by scission in the critical condition of degradation, decreases with the oscillatory frequency under the same critical imposed strain amplitude of 25%. Because shorter N_L can result in the degradation of one branched chain more than once, the branched chain can become further shorter one. That means the lower the value of Q_1 is, the more degradation occurs, which consists with our experimental results above.

At high frequency, the detail of degradation is different from that at low frequencies due to the different diffusion mechanisms of linear chains. The diffusive distance of P$_L$ is:

$$\Delta x_D(t) = \sqrt[4]{\delta^2 D^T t} \tag{17}$$

where D^T obeys the following formula:

$$D^T = D'_0\frac{1}{N_L} \tag{18}$$

and D_0 is also a constant. Then the scaling relationship between N_L and the oscillatory frequency and imposed strain amplitude should be:

$$N_L \propto f^{-1}\left(\sqrt{1+A\gamma_0} - B\right)^{-2} = Q_2 \tag{19}$$

The values of Q_2 at 9.425, 37.70 and 157.1 rad s^{-1} are also calculated with $A = B = 1$ and listed in Table 1. Within the range of high oscillatory frequencies, the degradation happens with the decreasing stain amplitude in linear regime as the frequency increases, which makes the length of linear scission part P$_L$ increase with the frequency. That means high shear rate increases the possibility of degradation at the sites approaching the branching points of LCB created by coupling reaction and also increases N_L.

4. Conclusions

Rheological measurements and LAOS followed FTR were successfully carried out to confirm the degradation occurring even with the strains applied within the linear viscoelastic regime of original PEB should be attributed to the LCB created in the reaction process. The applied strain amplitude and frequency have different effects on the degrading behavior of PEB chains. The oscillatory frequency determines the dynamics of polymer chains. Low oscillatory frequency allows the LCB fractions to relax; therefore, the strain amplitude is required to be out of linear regime of PEB to cause degradation. At higher oscillatory frequency, the LCB fractions are difficult to relax and diffuse, which then results in the degradation reaction even when the strain amplitude is in linear regime of original PEB. Moreover, there is a kind of selectivity of shear rate on the polymer chains for degradation. At low frequency the degradation is realized in the way of short scission segments but more than once. However, the possibility of degradation at the sites approaching the branching points of LCB created by coupling reaction increases at high frequency. Meanwhile, when the ordinary rheological tests cannot meet the requirement to judge whether there is degradation reaction, the FTR analysis following the LAOS experiments is one powerful and easy rheological methodology to do this.

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