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Polymer 47 (2006) 7051–7059

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The effect of shear flow on reaction of melt poly(ethylene-α-octene) elastomer with dicumyl peroxide

Jianye Liu, Wei Yu, Chixing Zhou*

Department of Polymer Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China

Received 9 May 2006; received in revised form 1 July 2006; accepted 8 August 2006
Available online 28 August 2006

Abstract

The reaction of melt poly(ethylene-α-octene) (POE) initiated by dicumyl peroxide (DCP) was studied at elevated temperature in both oscillatory and transient shear flow fields. In oscillatory shear flow, the storage modulus evolution was monitored by parallel plate rheometer with certain oscillatory frequencies and different strains, which were chosen to represent different flow fields. Our results indicated that at low frequencies (0.1 and 0.4 Hz) the dominant reaction was coupling with small strain amplitudes within the linear viscoelastic regime. However, the degradation, which was caused by β-scission of tertiary carbon macromolecular radicals, also occurred when large strains were applied, which were out of the linear viscoelastic regime. The threshold strain of degradation was only 8% at 1.5 Hz, still within the linear viscoelastic regime. The mechanisms of how the frequency and strain affected the degradation were different. On the other hand, in transient shear flow the degradation could hardly take place when the shear rate was lower than the critical value of 0.0025 s^{-1}. Moreover, the larger the shear rate, the more distinct was the degradation.

Keywords: POE; Shear flow field; Scission

1. Introduction

Ethylene-α-octene copolymers (POE) produced by constrained geometry catalyst technology from Dupont & Dow are a new family of polyolefins, which have recently received much attention because of their random comonomer distribution, a narrow molecular weight distribution and a controlled level of long chain branching (LCB) [1,2]. Due to the unique physical, rheological and mechanical properties, these new materials have been used to replace the conventional polyethylene. For some applications, such as foams, pipe, rotomolded articles, and wire and cable jacketing, the crosslinking reaction can be the perfect way to enhance the dimensional stability of POE at higher processing temperature.

There have been a number of publications about the modifications of polyolefins in the melt state by free radical methods, including irradiation and peroxide [2–15]. Polyethylene (PE), if treated with radical initiators, crosslinks easily but isotactic polypropylene (iPP), especially if treated with peroxyalcohols, degrades through a β-scission mechanism; crosslinking can be partially observed by using high amounts of peroxide or employing peroxides derived from aromatic acyl-peroxide. Until now, it has already been well established that the degradation was dominant in the reaction of the higher polyolefins such as polypropylene and polybutene with peroxide, and polyethylene- and ethylene-rich alpha-olefin copolymers were readily crosslinked, though scission may accompany crosslinking as the ethylene content decreased. The key factor seems to be the concentration of the tertiary carbons. As for POE with a few branched chains, the reaction might behave like that between PE and PP. When both scission and crosslinking were present, Claudia and Enrique [16] have found a mathematical kinetic

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* Corresponding author. Tel.: +86 21 54743275; fax: +86 21 54741297.
E-mail address: cxzhou@sjtu.edu.cn (C. Zhou).

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doi:10.1016/j.polymer.2006.08.013

model to predict the average molecular weight and the weight fraction of soluble parts for polymer chains subjected to irradiation, without shear flows. Johnston [17] concluded that the scission/crosslinking ratio of POE with DCP was 0.24 by a Monte Carlo simulation in a 160 °C RPA 2000 curemeter, but the details about the effect of shear field on the mechanism of reactions were not mentioned further. Also, other studies on the reactions of POE by free radical methods have been mainly limited to the investigation of the molecular and mechanical properties of chemically crosslinked POE as well as the effect of the experimental conditions such as the type and concentration of peroxide, the dose of the irradiation and temperature [5,6]. Anyway, little has been reported on the details of the reaction behavior in melt POE/peroxide system under the shear flow field.

So in the present research, a comparison of the reaction behaviors between different shear flows was conducted. Rheological tests, FTIR, NMR and GPC have been used to characterize a set of products. The main objective of this work is to check whether the dominant reaction in POE/peroxide is coupling or degradation, and then formulate the possible mechanisms as a function of the different shear flows applied in the reacting process.

2. Experimental

2.1. Materials

Ethylene-α-octene copolymer grade Engage8150, with octene content of 25 wt%, melt flow index of 0.5 g/10 min (190 °C, 2.16 kg) and density of 0.868 g/cm^3 (20 °C), was obtained from Dupont & Dow, USA. The data of molecular weight and the distribution of POE are listed in Table 1. Dicumyl peroxide (DCP, chemically pure), acetone (chemically pure) and xylene (a mixture of *o*-, *m*- and *p*-xylene whose boiling point is about 140 °C and density 0.87 g/cm^3 at 20 °C) were all purchased from Shanghai Chemicals Factory, PR China, and were used without any further treatment. The decomposition rate constant of DCP, k_d, is $3.67 \times 10^{-6}\ s^{-1}$ at 100 °C and $3.40 \times 10^{-3}\ s^{-1}$ at 160 °C, as provided by the supplier. The half-life time is 52.5 h and 204 s at 100 °C and 160 °C, correspondingly.

2.2. Sample preparation and rheological measurement

Pellets of POE (40 g) were impregnated with an acetone solution of DCP (0.15 g) over 12 h at room temperature. The solvent (acetone) was evaporated at a low pressure. And then the POE sample with DCP of 0.014 mol/kg was premixed in a torque rheometer (Haake Rheocord90, Germany) at 100 °C with a rotor speed of 60 rpm. The sample was taken out after 6 min and compressed into sheets (thickness ≈ 1 mm) at 100 °C under 12 MPa. We can consider that there was no reaction during the preparation, due to the long half-time of DCP at 100 °C (52.5 h). Then rheological tests were carried out on a rotating rheometer (Gemini 200HR, Bohlin Instruments, UK) with parallel plate geometry of 25 mm diameter. Both oscillatory and transient shear flows were applied at 160 °C with a gap of 1 mm between two parallel plates.

Table 1
Molecular weight and its distribution of the products

Samples	M_n (g/mol)	M_w (g/mol)	PDI[a]
POE	77 107	191 940	2.49
CS10	88 804	301 245	3.39
CS30	75 660	251 415	3.32
CS40	68 367	223 494	3.27
SS0025	84 459	269 702	3.19
SS004	84 155	273 200	3.24
SS01	79 624	261 417	3.28

[a] Polydispersity index.

The dynamic time sweeps for monitoring the reaction process were performed with a fixed frequency. However, it was not possible to follow the kinetics of the reactions at too low frequencies, because the measurement time must be significantly shorter than the time of change of the viscoelastic properties. Measurement frequencies of 0.1, 0.4 and 1.5 Hz were chosen here as the compromise between the low frequency needed to measure the equilibrium modulus and the high frequency needed to track the kinetics with good precision, as discussed by Mours and Winter [18]. For the cases at 0.4 Hz, the samples of tests with applied strain amplitudes from 5% to 40% were marked with *CS5*, *CS40* and so on, where *CS* signified the samples modified in oscillatory shear flow with 0.4 Hz and the number following it denoted the strain amplitude given in the test. The period of preparation, which included the time of heating, compressing the sample and stabilizing the temperature, was controlled as short as possible to minimize the reaction before rheological measurement. In order to make sure that the tests of *CS5*–*CS25* were always in linear viscoelastic regime, strain amplitude sweeps (Fig. 1) were applied for each fully modified POE at the same frequency. The objective of the tests with large strains (*CS30* and *CS40*), which were out of the linear regime, is to check the effect of the nonlinear shear flow (Fig. 1) on the reaction, and we observed that there was something different between the reactions in linear and nonlinear flows (Fig. 2). To check the effect of frequency on the

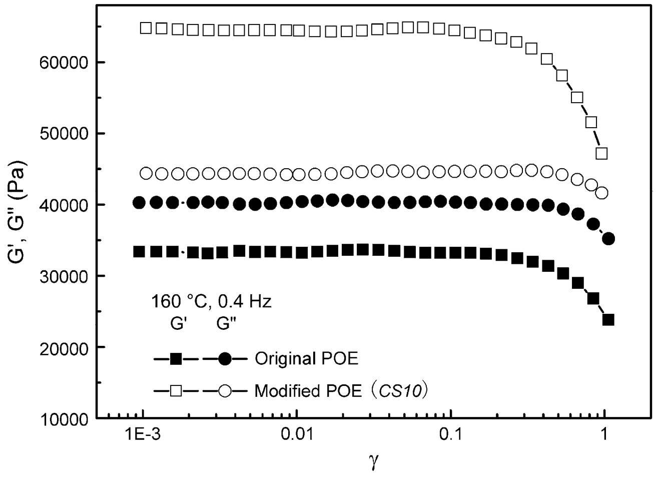


Fig. 1. Dynamic strain sweeps of original and modified POE (160 °C, $f = 0.4$ Hz).

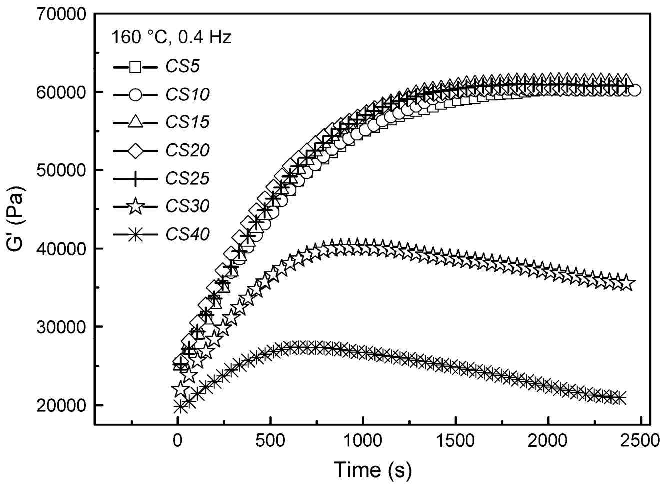


Fig. 2. Dynamic time sweeps at different applied strains (160 °C, $f = 0.4$ Hz).

degradation process, we carried out the tests at two other frequencies, 0.1 and 1.5 Hz, marked with "*BSx*" and "*DSx*", respectively, in which the letter *x* denoted the strain amplitude given in the test. All the experimental processes were the same as the tests at 0.4 Hz. On the other hand, we have also monitored the evolution of the reactions in transient shear mode, where the conformation of macromolecules would vary a great deal under such stronger shear flows. The shear rates were 0.001 s^{-1}, 0.0025 s^{-1}, 0.004 s^{-1}, 0.01 s^{-1} and 0.05 s^{-1}. In the same way, we labeled these tests with *SSx*, in which *SS* signified the samples modified in transient shear flow and the letter *x* still denoted the shear rates.

2.3. Purification and characterization

For all the tests on rheometer, the fully reacted samples were taken off for further FTIR, ^{13}C NMR, GPC and rheological measurements. Firstly, half of each reaction product was used to measure the gel contents employing Soxhlet extraction cycle for 24 h with xylene as the solvent at 120 °C, and there was no insoluble fraction left for each sample. So the complete dissolution of all reaction products in xylene indicated that no gels were created. The leftover part of each sample was also dissolved in xylene for purification. Afterwards, the resulting solution was added slowly into acetone, which was followed by filtration. Then the peroxide-modified POE was washed with acetone three times before drying in a vacuum oven at 50 °C for 48 h.

The resulting polymers were compressed into films (thickness ≈ 50 μm) at 100 °C under 12 MPa for FTIR measurements. The FTIR spectra were recorded by a Paragon 1000 FTIR spectrometer (Perkin–Elmer Inc., USA).

Solution ^{13}C NMR spectra were obtained on a MERCURY-plus 400 spectrometer (Varian Inc., USA) at 30 °C. A sample (25 mg) was dissolved in 0.5 mL of benzene-d_6 (C_6D_6) in a 5 mm diameter NMR tube. The ^{13}C NMR measurements of POE samples were performed at 100.63 MHz with the spectral width of 25 000 Hz (250 ppm), acquisition time of 1.2 s and data points of 60K. The chemical shifts were referred internally to that of the solvent carbon, which was 128.5 ppm. Distortionless enhancement of polarization transfer NMR (^{13}C NMR-DEPT) spectra was recorded with $J_{\mathrm{H-C}}$ of 140 Hz, a relaxation-relay time of 2 s, proton magnetic vector rotation angles $\theta = 135°$ giving CH's and CH_3's up, and CH_2's down.

The molecular weight and its distribution of original POE and completely reacted samples under different shear flow fields were determined at 30 °C by gel permeation chromatograph (GPC) instrument (Series 200, Perkin–Elmer Inc., USA), equipped with a set of three 10 μm columns, which were calibrated by narrow molecular weight distribution standards of polystyrene. The solvent used here was toluene with 1 mL/min flow.

The preparation of the product discs for rheological measurements followed the same way as mentioned above. The dynamic frequency sweeps of the products obtained in different shear flows were carried out on the same rheometer with parallel plate geometry of 15 mm diameter. The radian frequency range was from 0.01 to 100 rad/s with the given strain of 5%, which lay in the linear regime of all samples.

3. Results and discussion

3.1. Rheological evaluation

Because the storage modulus is sensitive to the mutation of the polymer network, it has been suggested that an increase in storage modulus was a measure of the chemical degree of transformation during curing [19] or crosslinking reactions [9]. The storage modulus (G') monitored here as a function of reaction time in the oscillatory shear flows with different strain amplitudes at 0.4 Hz is shown in Fig. 2. For small strain amplitude ($\gamma \leq 25\%$), the evolutions of G' are similar. Such strain amplitudes lie well in the linear regime in the period of oscillatory shear (Fig. 1). In the tests of *CS5–CS25* in the linear oscillatory shear flow, G' increased monotonously all the time and reached a similar plateau in the end, which is a result of the coupling reactions of two macroradicals leading to an increase in the degree of branching and an overall increase in the molecular weight of the system. Meanwhile, it can be further concluded that different strain amplitudes of oscillatory shear in linear regime have a little effect on the reaction rate of coupling in our system. The viscosities of the products of *CS5–CS25* fall into a single curve (Fig. 3), from which we conclude that there is no difference in the molecular weight as well as in the molecular weight distribution of the products. We have compared them with the product of *OS00*, which was obtained from the reaction without any shear flow (Fig. 4). The same level of molecular weight between them indicated that the case under weak shear flow was very similar to it in quiescent state. Moreover, the viscosities of the products of *OS00* and *CS5–CS25* were much higher than that of pure POE at low frequency, and coincide at high frequency. Since there were no gels formed in the samples, the increased viscosity at low shear rate and enhanced shear thinning could be likely attributed to the formation of long chain branch in the samples [20].

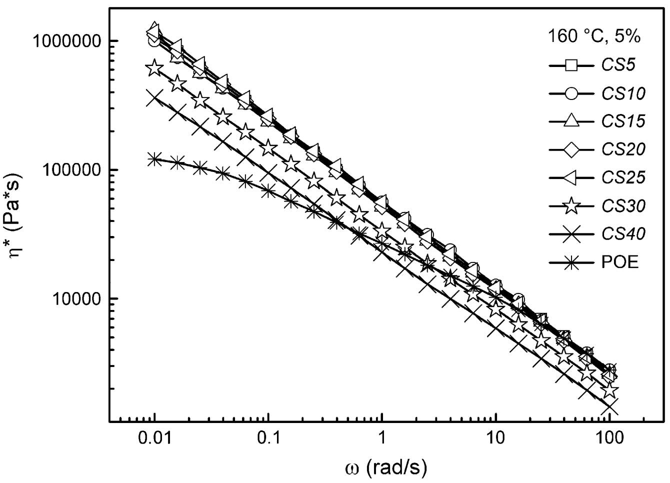


Fig. 3. Dynamic frequency sweeps of the products of *CS5*–*CS40* (160 °C, strain = 5%).

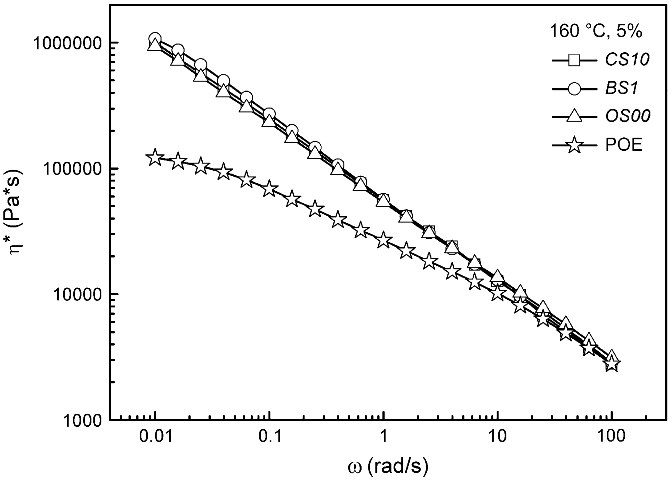


Fig. 4. Dynamic frequency sweeps of the products of *BS1*, *CS10* and *OS00* (160 °C, strain = 5%).

The strain amplitude starts to affect when it is out of the linear regime. The curves of *CS30* and *CS40* displayed that G' increased first and then decreased with time. This non-monotonic behavior is attributed to two possible reasons. Firstly, the linear regime changes during the experiment. A 30% strain amplitude lies in the linear regime and near the transition for pure POE, and moved into the nonlinear regime of the products as the reaction proceeded. This could possibly decrease the value of G' with time. Secondly, it is possible that the molecular weight of the system started to decrease after the apex, which was probably caused by the degradation reaction. In order to eliminate these effects of the nonlinearity, the dynamic frequency sweeps were applied on the fully reacted samples. From the frequency dependence of oscillatory complex viscosity η^* for the products of *CS30* and *CS40* in Fig. 3, two points could be observed. Firstly, the shear thinning was enhanced due to the creation of new topological structure (such as long chain branch) through the coupling reaction. Secondly, the overall η^* of both samples was much lower than the ones of the products gained in the tests with small strain amplitudes. This confirmed that the decrease in the molecular weight really happened under the oscillation with larger strain amplitude. Table 1 listed the molecular weight and its distribution of all the products. The conclusions from GPC with respect to the degradation of *CS30* and *CS40* are in accordance with the phenomena of decrease in complex viscosity. The experimental result at 0.1 Hz was very similar to the cases at 0.4 Hz (Figs. 5–7), and the critical strain amplitude to cause degradation was the critical strain of nonlinear regime (about 30%). We can also infer from *CS30*, *CS40* and *BS30*, *BS50*, *BS120* that the polymer chains degraded more and more as the strain amplitude deviated out of the linear regime. However, the critical strain to cause degradation changed when the frequency increased to 1.5 Hz. Figs. 8–10 showed the corresponding time sweep of reactants, the strain amplitude sweep and the frequency sweep of products, respectively. According to Figs. 8 and 10, the critical strain of degradation was only 8%. Such strain amplitude lies well in the

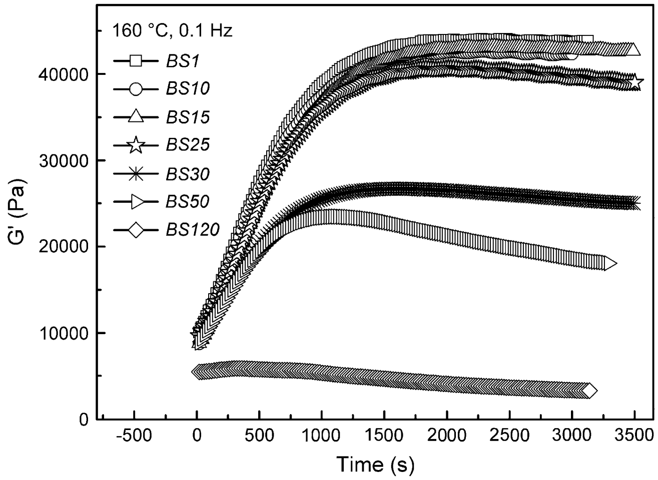


Fig. 5. Dynamic time sweeps at different applied strains (160 °C, $f = 0.1$ Hz).

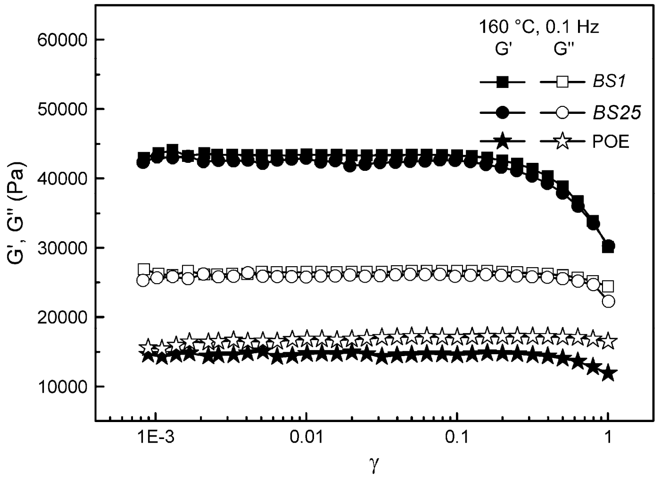


Fig. 6. Dynamic strain sweeps of original and modified POE (160 °C, $f = 0.1$ Hz).

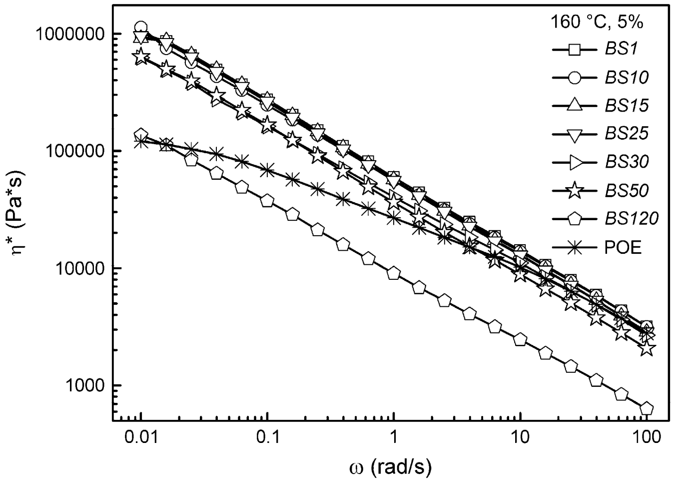


Fig. 7. Dynamic frequency sweeps of the products of *BS1–BS120* (160 °C, strain = 5%).

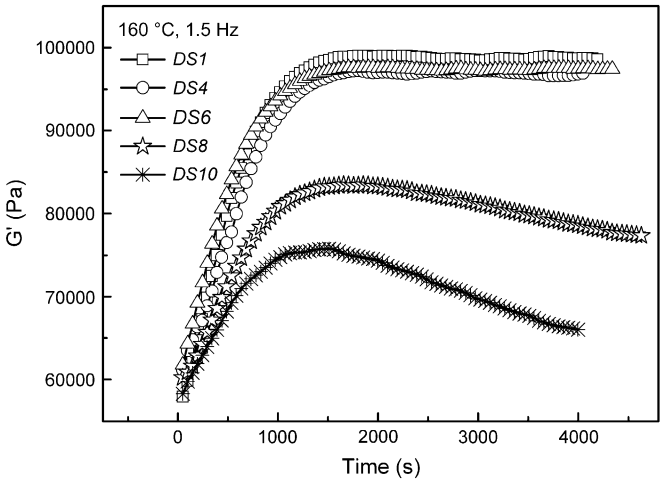


Fig. 8. Dynamic time sweeps at different applied strains (160 °C, *f* = 1.5 Hz).

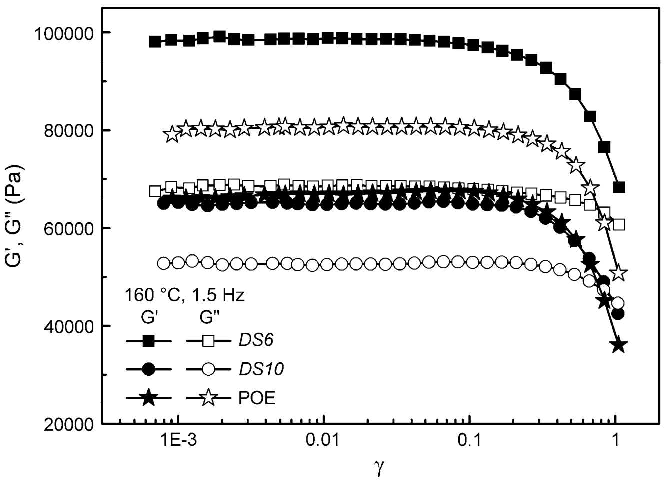


Fig. 9. Dynamic strain sweeps of original and modified POE (160 °C, *f* = 1.5 Hz).

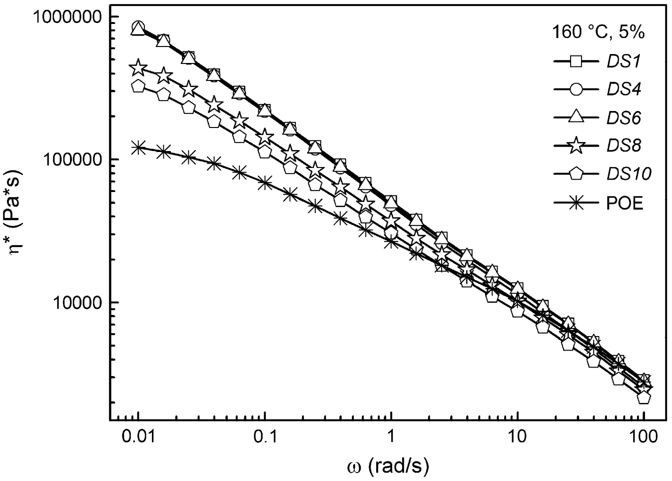


Fig. 10. Dynamic frequency sweeps of the products of *DS1–DS10* (160 °C, strain = 5%).

linear regime of all samples. This fact revealed that compared with the strain, the frequency owned a different acting mechanism to cause the degradation reaction.

On the other hand, we used the transient viscosity η to follow the course of the reaction. The transient time sweeps of *SS001*, *SS0025*, *SS004*, *SS01* and *SS05* and the dynamic frequency sweeps of the corresponding products are shown in Figs. 11 and 12, respectively. Under the smallest shear rate (0.001 s^{-1}), there is no evident decrease of viscosity during the reaction. The shear viscosity and molecular weight show that the product of *SS001* is very close to those under small amplitude oscillatory shear flow (*CS10*), which means only coupling reaction is possible. When the shear rate was 0.0025 s^{-1}, the behavior of decrease in viscosity similar to the situations in *CS30*, *DS30* and *BS8* appeared. This could be accounted for the degradation accompanying the coupling reaction. Moreover, the higher the shear rate, the lower were the viscosity and the molecular weight (Table 1). So high shear rate is beneficial to the degradation. The difference between the

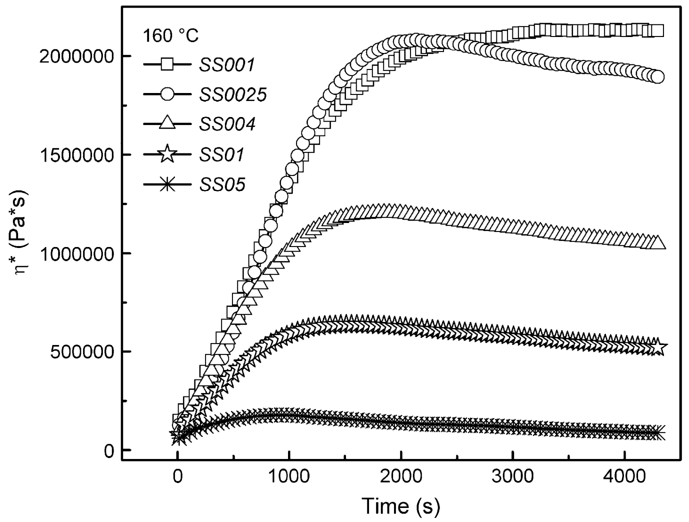


Fig. 11. Transient time sweeps with different shear rates (160 °C).

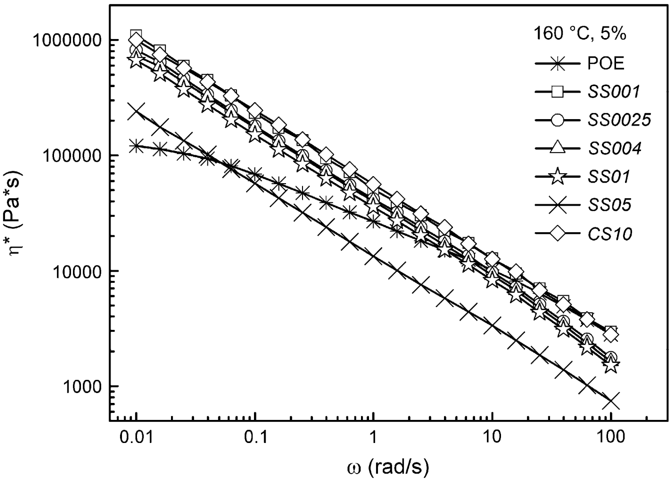


Fig. 12. Dynamic frequency sweeps of the products of *SS001–SS05* (160 °C, strain = 5%).

oscillatory shear and transient shear is that possible degradation could happen in transient shear even under rather weak shear. The smallest shear rate (*SS0025*, $\dot{\gamma} = 0.0025\ \mathrm{s}^{-1}$) in transient shear tests that showed possible degradation was much smaller than the maximum shear rate in the oscillatory shear tests of *BS30* ($\dot{\gamma}_{\max} = \omega\gamma_0 = 0.188\ \mathrm{s}^{-1}$), *CS30* ($\dot{\gamma}_{\max} = \omega\gamma_0 = 0.754\ \mathrm{s}^{-1}$) and *DS8* ($\dot{\gamma}_{\max} = \omega\gamma_0 = 0.754\ \mathrm{s}^{-1}$). From this point of view, transient shear seemed to have more evident effects on the degradation reaction than the oscillatory shear flow.

3.2. FTIR and GPC measurements

The reaction products haven't turned yellow and IR measurements have been also made to confirm whether oxidation in air occurred during the modification of POE with DCP. By comparing the FTIR spectra of sample of *SS05* and the original POE, which are shown in Fig. 13, no new absorption peak is observed. The number of the carbonyl groups was probably too low to be observed, even if there has been oxidation in the reaction. So we considered that the degradation was not mainly caused by the oxidation in air.

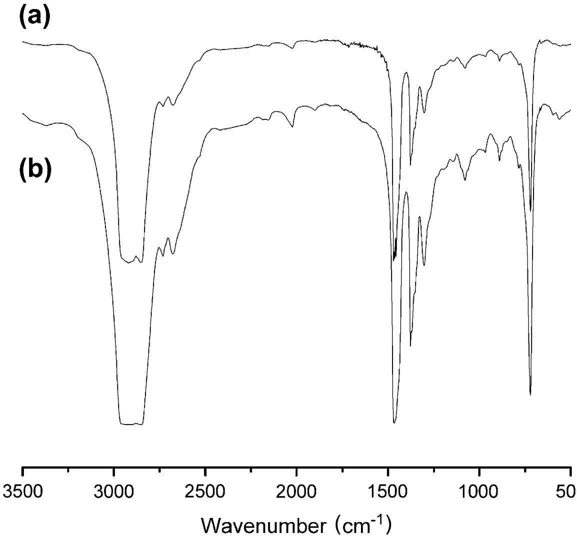


Fig. 13. FTIR spectra of: (a) the original POE and (b) the products of *SS05*.

The molecular weight data of the products are listed in Table 1, and the corresponding GPC data describing the molecular weight distributions (MWD) of the original POE and the products of *CS10*, *CS40* and *SS01* are displayed in Fig. 14. It can be seen that the curves of *CS40* and *SS01* shift to higher elution times (lower molecular weights). These indicate that the degradation truly occurred during the modification compared with the case of *CS10*, which is consistent with the results of rheological measurements demonstrated above. Moreover, the respective MWD of *CS40* and *SS01* gets broader than the original one due to the reaction.

3.3. ^{13}C NMR and DEPT

The 100.63 MHz ^{13}C NMR spectrum of the original POE is illustrated in Fig. 15, with assignments according to the previous result proposed by Pooter et al. [21], but the resonance line at 35.26 ppm, whose intensity reduced in the ^{13}C NMR

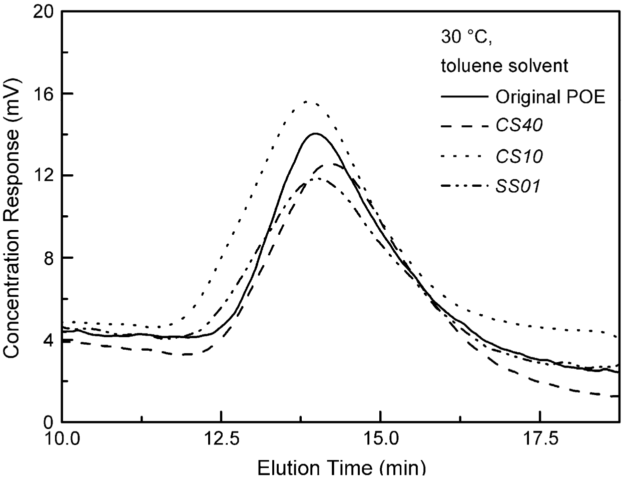


Fig. 14. Molecular weight distributions by GPC of the original POE and the products of *CS10*, *CS40* and *SS01* (30 °C, in toluene).

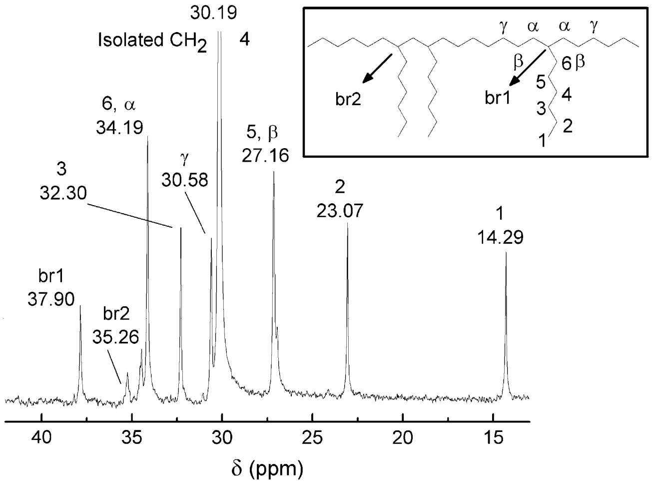


Fig. 15. The ^{13}C NMR spectrum of original POE.

spectrum of the POE that suffered from degradation (Fig. 16), has not been assigned to any structure. By the DEPT spectrum (Fig. 17), this signal should come from the tertiary carbon atoms, which are different from the ones with the chemical shift at 37.90 ppm. So we labeled these two kinds of branching points with br1 and br2, respectively. The chemical shift, δ, for the tertiary carbon atoms can be estimated on the basis of the method for the saturated alkanes [22].

$$\delta = -2.6 + 9.1n_\alpha + 9.4n_\beta - 2.5n_\gamma + S_2 + S_3 \qquad (1)$$

where α, β and γ refer to the positions of carbons on both sides of the branch, and n_α, n_β and n_γ are the numbers of the corresponding carbons. The value of −2.6 is the δ value for methane, and the correction terms have usual meanings for tertiary carbons: $S_2 = -3.7$ and $S_3 = -9.5$. Considering the chemical shift difference between these two kinds of branching points, which is nearly 2.5, we infer that the reason why the chemical shift of tertiary carbons in the structure br2 moved towards the high field is that there is one more substitution at β position of isolated tertiary carbons. This is consistent with the known fact that there was polymerization process of POE as follows: $R{-}C_8{-}Cat + C_8 \rightarrow R{-}C_8{-}C_8{-}Cat$ [1].

On the other hand, the resonance intensity of the tertiary carbons in the structure br1 changed little. Therefore, the key factor favoring tertiary carbons as sites for scission is the distance between branches. The chain scission is possible only when there are two tertiary carbons in a chain separated by only one CH_2 group, while the isolated tertiary carbon radical (br1) cannot undergo scission due to the product of a primary radical, which seems unfavorable (Scheme 1). This conclusion is consistent with Sajkiewicz's [12]. And we can understand well that polypropylene and polystyrene are easy to degrade with peroxide, while polyethylene doesn't behave like this even with some branches in the structure br1.

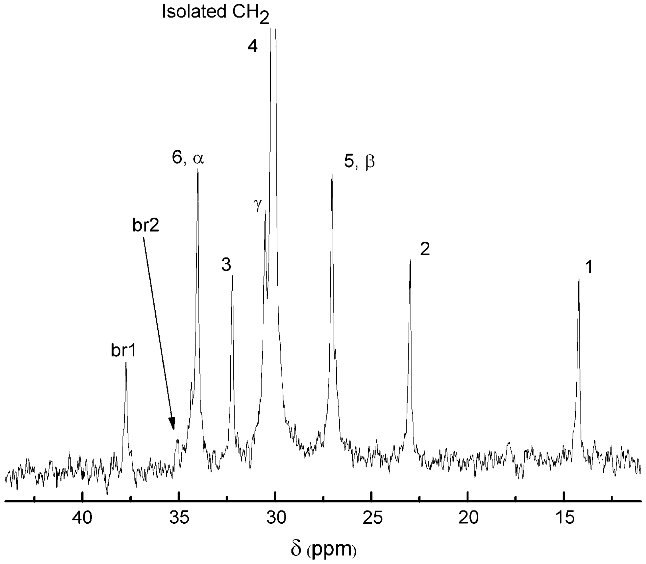


Fig. 16. The ^{13}C NMR spectrum of degraded POE (*SS05*).

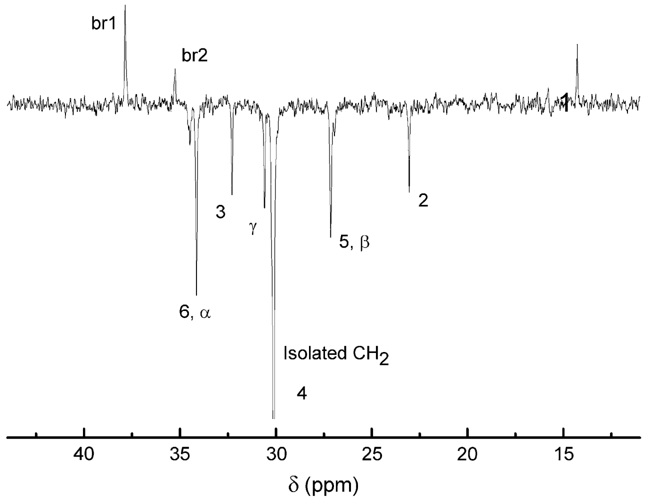
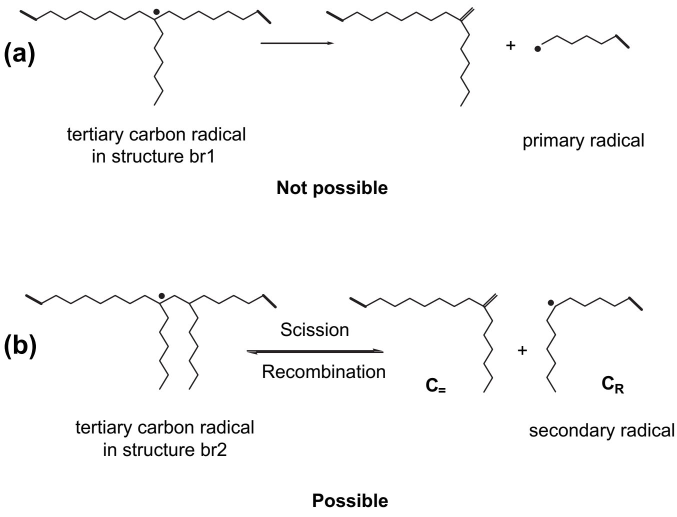


Fig. 17. The ^{13}C NMR-DEPT 135° spectrum of original POE.

3.4. Proposed mechanism for degradation of POE chains in shear flow fields

Since β-scission, a kind of monomolecular reaction, is attributed to the chemical and structural properties of the tertiary carbon radicals, it is independent of the shear flow field. We consider that it could also occur even in quiescent state. But the counter reaction, 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 (Scheme 1), can be affected by the shear flow field greatly in such entanglement system. de Gennes [23] demonstrated that when two reactive sites approach within a "capture radius" *a*, an instantaneous and irreversible reaction occurs. So it is the relative distance between two neighboring chains produced by β-scission that determines whether the degradation could be induced or not.

In quiescent state or the weak shear flow field, two reactive sites (C_R and $C_=$) can be separated only by diffusion. Since no



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

degradation could be observed in the almost quiescent state, it is believed that the recombination rate is much larger than the reciprocal of the Rouse time, which is the time scale for the reaction sites to diffuse away from each other over a distance of about the tube diameter. On account of the shear flow, the distance between the macromolecular radicals and the polymer chains with a double bond could exceed the range of radius *a*, which results in degradation.

Because the relative distance between two neighboring chains produced by β-scission determines whether the degradation could be induced, this degradation process is controlled by micro-diffusion and macro-convection, on which the distance between C_R and $C_=$ depends. And this displacement at time *t* under the simple shear flow $\mathbf{\Gamma}$ can be estimated by

$$\vec{\mathbf{x}}(t) = \exp(\mathbf{\Gamma}\cdot t)\cdot\vec{\mathbf{x}}_0 + [\vec{\mathbf{x}}_D(t) - \vec{\mathbf{x}}_0] \qquad (2)$$

where $\vec{\mathbf{x}}_0$ is the original displacement between C_R and $C_=$, $\exp(\mathbf{\Gamma}\cdot t)\cdot\vec{\mathbf{x}}_0$ is the displacement at time *t* if they moved only by advection and $\vec{\mathbf{x}}_D(t)$ is the displacement at time *t* if they moved only by diffusion and holds for $\vec{\mathbf{x}}_D(0) = \vec{\mathbf{x}}_0$. The advection of flow can separate the reactant, while the diffusion can bring them together. According to de Gennes [23], the relationship between the diffusive distance and time is

$$\Delta x^2(t) = 2D_{\mathrm{rep}}t \quad (t > t_{\mathrm{rep}}) \qquad (3)$$

or

$$\Delta x^4(t) \sim t \quad (t_R < t < t_{\mathrm{rep}}) \qquad (4)$$

where D_{rep} is the macroscopic diffusion coefficient, and t_R and t_{rep} are the Rouse time and reptation time, respectively. Here we consider that one of the fragment chain, either C_R or $C_=$, is linear and much smaller than the original one.

In oscillatory shear flow the relative distance changes in a limited range. Based on the above, both the frequency and the strain can affect the distance created by convection. Besides this, the former also has the effect on the diffusive distance because the strain increases with time *t* only in the half period of oscillation. The reptation time of linear chain of POE is of the order 10^{-1} s, which corresponds to a critical frequency of more than 0.5 Hz. When the applied oscillating frequency is smaller than the critical one (such as 0.1 and 0.4 Hz in our experiments), the two combinable chains have sufficient time to relax during this time *t*. Here the diffusion played an important role ($\Delta x(t) \sim t^{1/2}$) when the small strains were carried out. Only sufficiently large strain can separate the C_R and $C_=$ chains. Degradation could occur just when the strain is out of the linear viscoelastic regime. But for larger frequency (1.5 Hz), degradation also occurred even though the strain was still within the linear viscoelastic regime. The time for unidirectional shear was smaller than the reptation time of linear chains and not enough for the C_R and $C_=$ chains to relax. The effect of diffusion is quite limited ($\Delta x(t) \sim t^{1/4}$). Shear flow becomes the dominant part that led to degradation with the small strain of 8% in linear regime, and it could also be inferred that the critical strains for degradation would decrease in the cases at higher frequencies.

In transient shear flow, the effect of shear and diffusion can be understood by the local Peclet number, which is defined as $Pe = \dot{\gamma}a^2/D_{\mathrm{rep}}$ [24]. The convection becomes dominant when $Pe > 1$. It is acceptable that the "capture radius" *a* is smaller than or at most comparable to the tube diameter, and for an entangled polymer, tube diameter is of the order of some nanometers, the diffusion coefficient is about 10^{-18} m^2/s, which is estimated by $D_{\mathrm{rep}} = k_BT/3N^2\zeta$. So the shear rate should be close to 10^{-2} s^{-1}. Although the quantitative value is not correct, it is still reasonable to conclude that diffusion can only be important at very small shear rate.

So there should be a threshold in shear flow near which degradation begins to dominate. In transient shear flow, shear rate is the only dominant factor, which is required to be at least 0.0025 s^{-1} to cause degradation. In oscillatory shear flow, both frequency and strain amplitude affect degradation. A critical frequency exists below which the degradation could happen only when the strain is out of linear regime. Small strain amplitude in linear regime can cause degradation when the applied frequency is sufficiently high.

4. Conclusions

The starting points of this study were to determine whether the dominant reaction in the system of POE initiated by peroxide is coupling or degradation and to investigate the effect of the shear flow field on such reactions. Firstly, our ^{13}C NMR results revealed that not all kinds of the tertiary carbon radical are able to undergo β-scission. The chain scission is possible when there are two tertiary carbons in a chain separated by only one CH_2 group (structure br2).

Notably, the reaction of degradation didn't occur in quiescent state or weak shear flow. However, different shear flows have distinct effect on the degradation reactions. Transient shear flow can increase the distance between C_R and $C_=$ when the shear rate is large enough to ignore the diffusion of polymer chains ($Pe > 1$). The magnitude of shear rate is the only decisive factor in transient shear flow. However, both frequency and strain amplitude in oscillatory shear flow could affect the degradation. The applied frequency determines the dynamics of polymer chains. Low oscillating frequency allows chain to relax and diffusion is much faster. Therefore, the strain amplitude is required to be out of linear regime to cause degradation. Under higher oscillating frequency, the chain is hard to relax and difficult to diffuse, which results in the degradation reaction even when the strain amplitude is in linear regime. Therefore, the degradation of POE is regarded to be easier in transient shear than in oscillatory shear flow.

Acknowledgements

The authors thank financial support for this work from the National Science Foundation of China (No. 50390090 and No. 20574045).

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