

Thermal Oxidation of Metallocene-Catalyzed Poly(ethylene octene) by a Rheological Method

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ABSTRACT: The thermal oxidation of a metallocene-catalyzed poly(ethylene octene) (POE) melt was studied by a dynamic rheological method. Furthermore, to prove the effect of oxygen on the thermal oxidation of POE, cyclic samples, which consisted of virgin POE in the outer circle and POE with antioxidant inside, were made. The results showed that a thermal-oxidation-induced crosslinking reaction occurred in the POE melt at a high temperature. The amount of the antioxidant determined the thermal oxidation of POE when the

antioxidant was added, and the diffusion of oxygen controlled the thermal oxidation of POE without the antioxidant. In addition, Fourier transform infrared and gel content characterization confirmed that the crosslinking occurred and that carbonyl groups formed in the reaction. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 846–852, 2007

Key words: antioxidants; diffusion; elastomers; rheology; viscoelastic properties

INTRODUCTION

The recent developments of constrained-geometry metallocene catalyst technology have made it possible to synthesize copolymers of ethylene and α -olefin with narrow molecular weight distributions and homogeneous comonomer distributions.¹ This new technology has produced a variety of polyolefins, including polyolefin elastomers such as poly(ethylene octene) (POE). POE is aimed at competing with conventional thermoplastic elastomers, such as ethylene propylene diene monomer (EPDM), in the automobile industry.² There are lots of published reports on the mechanical, thermal, and rheological properties of POE.^{1,3–9}

Polyethylenes differ in their densities, types and extents of branching, and types and amounts of double bonds, depending on the polymerization process used commercially. Linear low-density polyethylene mainly includes Ziegler-type and metallocene-type polyethylenes. The structural differences, as well as the processing conditions, play a significant role in determining the types of oxidative reactions. Generally, Ziegler-type polyethylene predominantly undergoes crosslinking reactions and the enlargement of the molecular weight, particularly at low temperatures. However, the importance of a chain scission reaction becomes more pronounced at higher temperatures. In the past, a large number of works about thermal oxidation and stabiliza-

tion were devoted to conventional Ziegler-type polyethylene.^{10,11} However, only a limited number of studies of the new metallocene-catalyzed polyethylene have been found in the literature. As far as we know, only Hoang et al.^{12,13} have investigated the thermal oxidative stability of different metallocene-catalyzed polyethylenes both in the solid state and in the melt state.^{12,13} In the solid state, the results showed that the metallocene-catalyzed polyethylenes exhibited outstanding thermal oxidative stability, which might be attributed to the low concentrations of innocuous catalyst residues together with the low initial vinyl unsaturation and short-branching contents. In the melt state, the results indicated that crosslinking reactions prevailed in the early stages of the degradation of mastication for most polymers, and the width of the molar mass distribution curve played an important role in influencing the initiation stages of oxidative degradation.

Small-amplitude oscillatory shear flow is very sensitive for detecting the structural transformation, long-branching content, and morphology evolution of polymers because its strain is too small to destroy the structure of a polymer.¹⁴ Besides, it is a good tool for studying chemical reactions.^{15–17} Wu and coworkers studied the correlation between oxidation-induced crosslinking and the dynamic rheological behavior of high-density polyethylene¹⁸ and high-density polyethylene/carbon black (CB) composite melts.¹⁹ Cao et al.²⁰ studied the relationship between the thermal oxidation and rheological behaviors of EPDM. However, few studies have reported the thermal oxidation of metallocene-catalyzed POE using a rheological method. In this study, small-amplitude oscillatory shear flow was used to study the thermal oxidation of POE.

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TABLE I
Characteristics of Metallocene-Catalyzed POE

	Density (g/cm ³)	Octene (wt %) ^a	Branch content (CH ₃ /1000 C) ^a	M _w (g/mol) ^b	M _n (g/mol) ^b	M _w /M _n
POE	0.868	25	32	191,940	77,107	2.5

^a Determined by means of ¹H-NMR and ¹³C-NMR.⁴

^b Determined by high-temperature gel permeation of chromatography.

EXPERIMENTAL

Studies were performed on metallocene-catalyzed POE. POE is a copolymer of octene and ethylene with 25 wt % 1-octene (Engage 8150); it was obtained from DuPont/Dow Chemical Co. (Wilmington, DE; Midland, MI). The characteristics are listed in Table I. The virgin POE was called POE (Pure). POE with 1 wt % antioxidant Irganox 1010, called POE(Antioxidant), was processed in a Haake Rheocord (Rheology Solutions Pty. Ltd., Bacchus Marsh, Victoria, Australia) 90 internal mixer. The temperature of the mixing chamber was set at 180°C, and the processing time was 8 min. The rotor rate was set at 60 rpm. Specimens for rheological testing were prepared at 180°C through the molding of disks about 1 mm thick and 25 mm in diameter, which were designed to match the plate diameters employed in the rheometer.

The rheological characterization of POE was carried out with a rotational rheometer (Gemini 200 HR, Bohlin Instruments, Malvern, UK). A parallel-plate configuration was used with a gap of about 1.0 mm and a plate diameter of 25.0 mm. The samples were subjected to a small-amplitude oscillatory shear flow in the linear viscoelastic regime at a strain of 5%. All the rheological tests were performed under an air atmosphere.

Functional group formation was measured by Fourier transform infrared (FTIR) spectrophotometry with a film prepared by compression molding at 100°C. The spectrometer was a Paragon 1000 (Perkin-Elmer, Inc., Piscataway, NJ).

The weighed samples, which were subjected to a small-amplitude oscillatory shear flow in the linear viscoelastic regime at a strain of 5% and a single frequency of 0.1 rad/s for 2 h, were put into boiling xylene for 48 h. Then, the extracted samples were dried to a constant weight in a vacuum oven at 60°C for 2 days. The gel content was expressed as a percentage of the remaining weight.

RESULTS AND DISCUSSION

Rheological characterization of the thermal oxidation of POE

To investigate whether the degradation had taken place in the blender, we checked the rheology of the

fresh sample of virgin POE that had not gone through the blender, POE conditioned in the blender but with the antioxidant added, and POE with the antioxidant conditioned in the blender. The results are shown in Figure 1. The storage modulus (G') and complex viscosity (η^*) show excellent agreement between the results, suggesting that the influence of the conditioning process on POE could be negligible.

The thermal stability of POE can be readily examined by temperature ramp experiments. POE(Pure) and POE(Antioxidant) were heated at 1.5°C/min

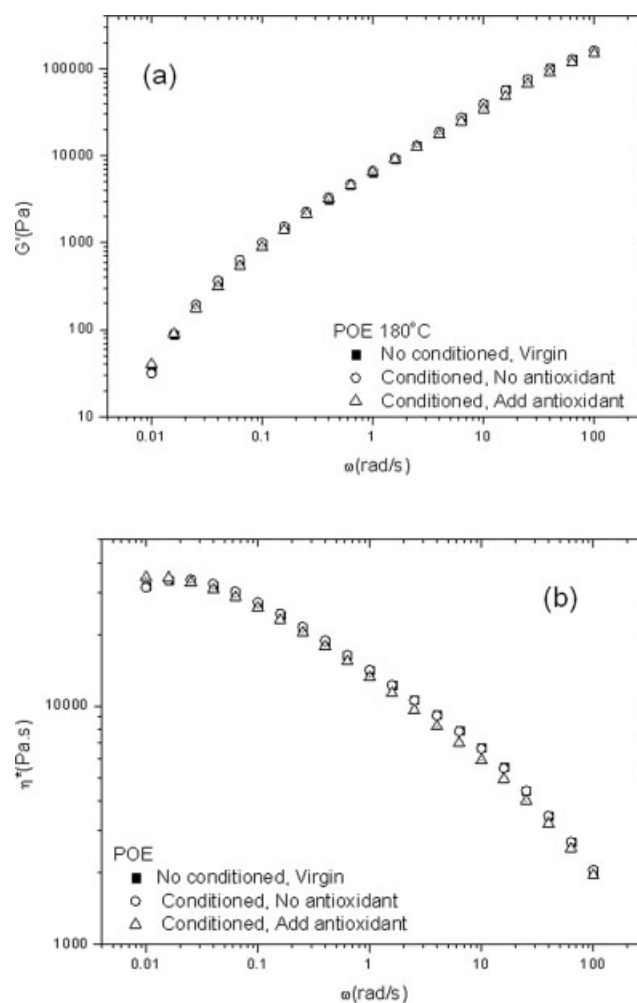


Figure 1 Isothermal frequency sweep at 180°C: (a) G' and (b) η^* .

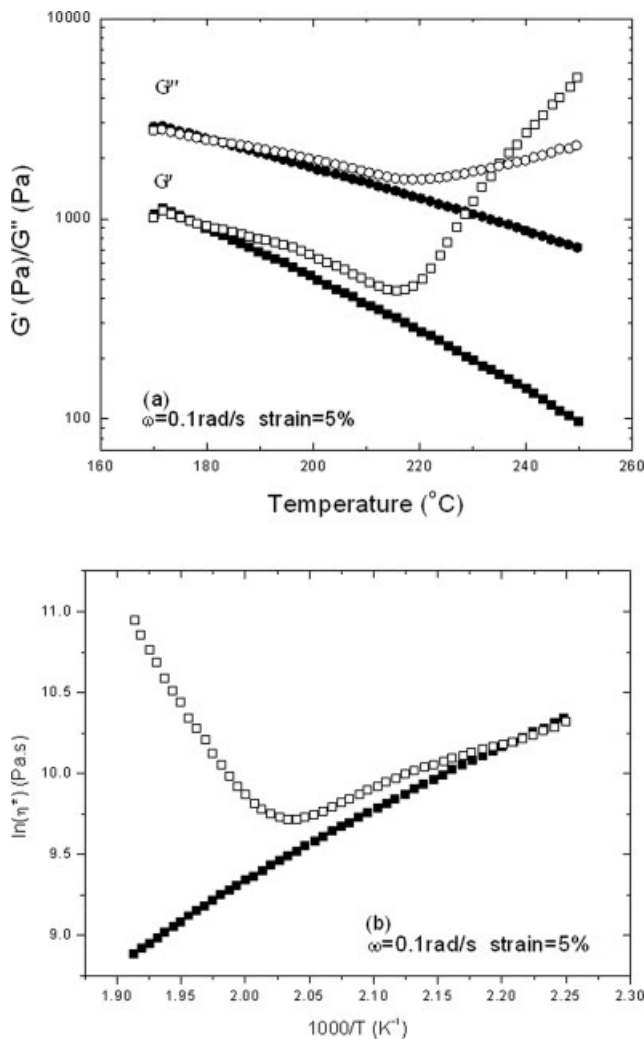


Figure 2 Temperature ramp of POE at a frequency of 0.1 rad/s and a heating rate of 1.5°C/min for (○) POE(Pure) and (●) POE(Antioxidant): (a) G' and G'' versus temperature and (b) Arrhenius plots of η^* versus $1000/T$.

from 170 to 250°C while G' , the loss modulus (G''), and η^* were measured at a single frequency of 0.1 rad/s. The results are shown in Figure 2. Temperature ramps with and without autogap control were performed, and the thermal compensation on the gap had little effect on the measured results. Only the results without the autogap control are shown in Figure 2. It is clear that G' , G'' , and η^* of POE(Pure) decrease with increasing temperature until a sharp increase at about 220°C. However, with respect to POE(Antioxidant), both the modulus and viscosity decrease continuously with the increase in the temperature, and there is no sharp transition. It is known that the modulus and viscosity of pure polymers are related to the molecular weight and molecular structure of the polymer chains. The sharp increase in G' , G'' , and η^* may be attributed to the increase in the molecular weight due to the thermal oxidation of POE in a molten state. To verify the

results, an isothermal frequency sweep with the angular frequency ranging from 0.01 to 100 rad/s at different temperatures was performed on POE(Pure) and POE(Antioxidant). The results at 220°C are shown in Figure 3. The viscoelastic properties in a low frequency range can indicate the change in the molecular structure of POE sensitively. G' of POE(Pure) in a low frequency range is larger than that of POE(Antioxidant), and a characteristic feature of a plateau zone appears. Interestingly, the loss tangent ($\tan \delta$) of POE(Pure) passes through a minimum first and then goes through a maximum, as can be seen in Figure 3. However, in POE(Antioxidant), the characteristic feature of the plateau zone vanishes and $\tan \delta$ decreases with increasing angular frequency. The changes in G' and $\tan \delta$ of the polymer without any structural transformation are like those of POE(Antioxidant), to which the antioxidant was added. Therefore, we can conclude that the characteristic feature of POE(Pure) is caused by thermal ox-

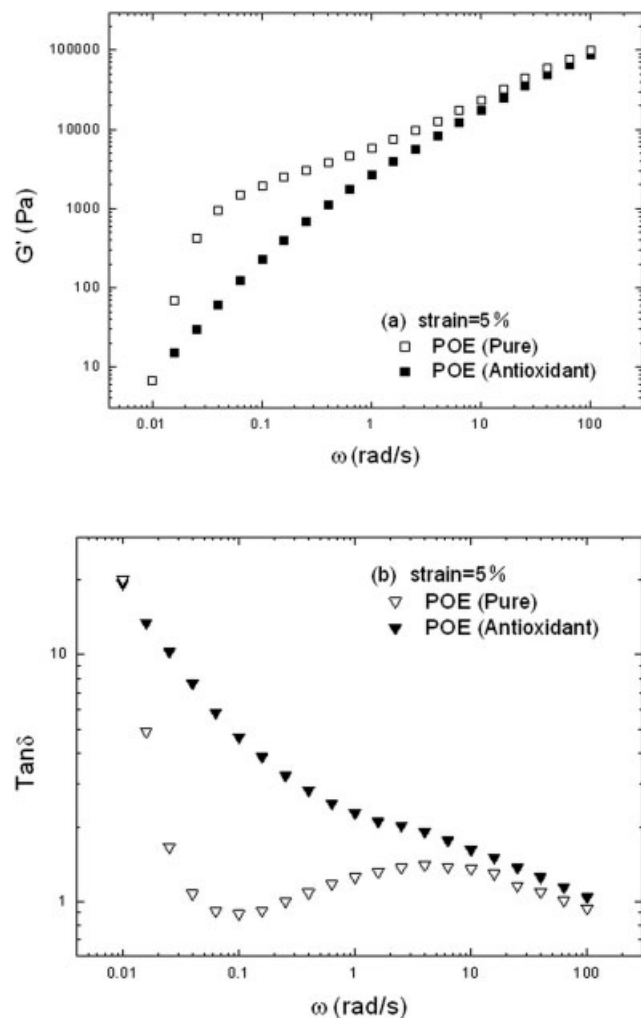


Figure 3 Viscoelastic properties of POE(Pure) and POE(Antioxidant) as a functions of the frequency (ω) at 220°C: (a) G' and (b) $\tan \delta$.

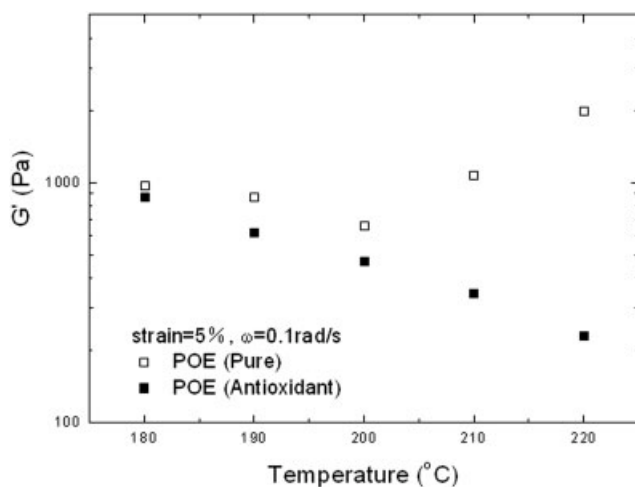


Figure 4 G' at the angular frequency of 0.1 rad/s, selected from isothermal frequency sweeps at different temperatures.

idation. In addition, G' values at the angular frequency of 0.1 rad/s were selected from isothermal frequency sweeps at different temperatures from 180 to 220 °C. The results, shown in Figure 4, are in agreement with the temperature ramp experiments in Figure 2.

To study the relationships between the viscoelasticity and time, the samples were subjected to a small-amplitude oscillatory shear flow at the single frequency of 0.1 rad/s while η^* was monitored with time. As shown in Figure 5, η^* of POE(Pure) increases quickly with time, and this reveals the existence of chemical reactions. The changes in G' and G'' are similar to the change in η^* . However, after the antioxidant is added to virgin POE, the change in η^* is totally different. η^* of POE(Antioxidant) is almost constant until the critical time (experimental time) of 2833 s, and this implies that the antioxidant

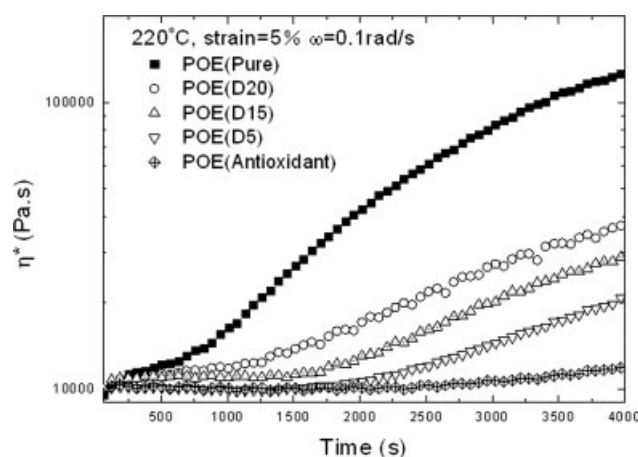


Figure 5 η^* as a function of time at the single frequency of 0.1 rad/s at 220 °C.

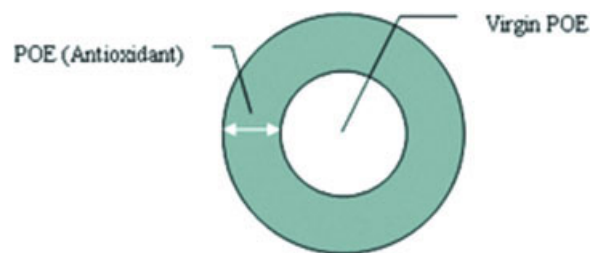


Figure 6 Scheme of the cyclic samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

inhibits the chemical reactions. That is, the increase in η^* of POE(Pure) results from thermal oxidation, which demonstrates our previously mentioned assumptions.

Because all the experiments were performed in an air atmosphere and some previous work has shown that thermal oxidation under an N_2 atmosphere can be greatly inhibited,^{18–20} it is interesting to know the effect of oxygen on the thermal oxidation of POE. To prove the effect of oxygen on the thermal oxidation of POE, cyclic samples were made, as shown in Figure 6. Virgin POE (without the antioxidant) was surrounded by POE with antioxidant 1010. The diameter of the whole round disk, which was composed of virgin POE and POE with the antioxidant, was 25 mm. The samples containing virgin POE with diameters of 20, 15, and 5 mm were called POE(D20), POE(D15), and POE(D5), respectively. The cyclic samples were subjected to a small-amplitude oscillatory shear flow at the single frequency of 0.1 rad/s while η^* was plotted in Figure 5. η^* is nearly constant until a sharp increase at about 1008 s for POE(D20), at about 1827 s for POE(D15), and at about 2406 s for POE(D5). The increase in the viscosity can be regarded as the start of crosslinking by thermal oxidation. Because the pure POE is surrounded by POE with the antioxidant and has no direct contact with oxygen, there are two possible reasons for the thermal oxidation in the sample: the diffusion of the oxygen into the virgin POE and the exhaustion of the antioxidant in the outer circle.

FTIR and gel content characterization

Infrared spectroscopy was the method of choice for detecting changes and the chemical nature of the products formed in the oxidizing polymers. Figure 7 presents the FTIR spectra of virgin POE and the different parts of virgin POE after rheological tests for 30 min. The absorption maximum at 1718 cm^{-1} in Figure 7(c) is attributed to the formation of carbonyl groups¹⁰ because the edge of the sample is in direct contact with air. In contrast, there is no absorption peak near 1718 cm^{-1} in Figure 7(a,b). The results

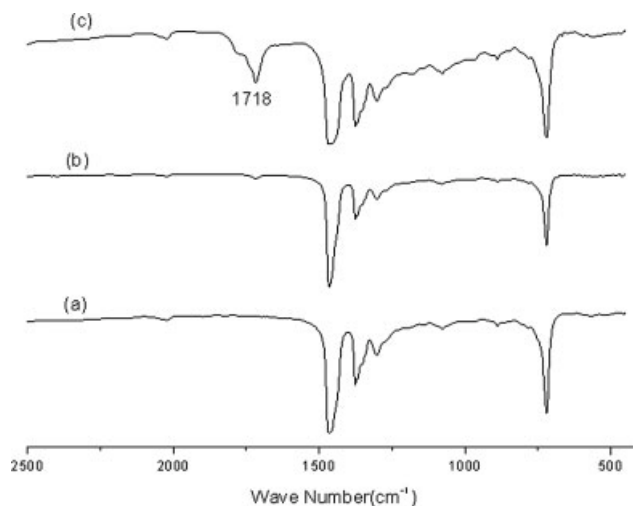


Figure 7 FTIR spectra: (a) virgin POE, (b) the center of POE(Pure) subjected to small-amplitude oscillatory shear flow at the single frequency of 0.1 rad/s for 30 min, and (c) the edge of virgin POE subjected to small-amplitude oscillatory shear flow at the single frequency of 0.1 rad/s for 30 min.

indicate that thermal oxidation occurs in the edge of the sample and that carbonyl groups form. However, in the center of the sample, there is no carbonyl group. Similarly, the FTIR results for POE(D15) (Fig. 8), POE(D20), and POE(D5) also show that carbonyl groups form at the edge of the samples, but no functional groups form in the center. The results indicate that the thermal oxidation occurs only at the edge of the samples, and this tells us that the chemical reactions control the thermal oxidation for the cirque samples. This conclusion agrees well with the rheological results.

The gel contents of the samples subjected to a small-amplitude oscillatory shear flow in the linear viscoelastic regime at the strain of 5% and single frequency of 0.1 rad/s for 2 h were measured. The results are listed in Table II. The gel content of POE(Pure) is only 4.53%, which is very small. In POE(Antioxidant), there is no gel formed. The results suggest that thermal-oxidation-induced crosslinking reactions happen at the edge of POE(Pure), which is in contact with air, and the antioxidant inhibits the thermal-oxidation-induced crosslinking reactions.

Process analysis

It has been shown that the oxidation process of polyolefins can be well monitored by rheology. For pure POE, the viscosity increases almost at the beginning. Although it is clear that oxygen could be involved in the oxidation reaction, it is still unknown which factor is the decisive one in the oxidation, that is, the

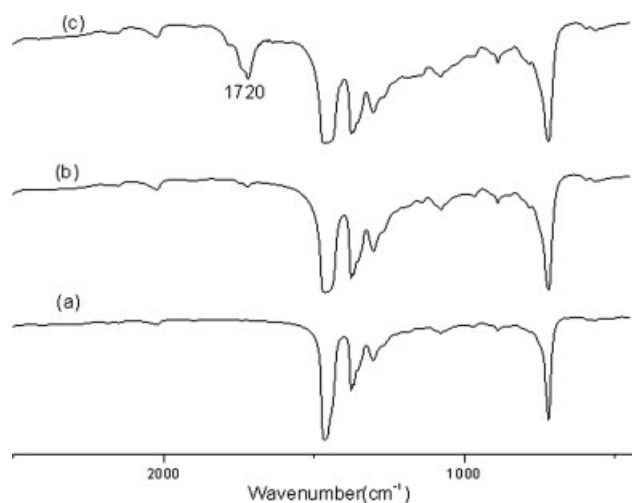


Figure 8 FTIR spectra: (a) POE(Pure), (b) the center of POE(D15) subjected to small-amplitude oscillatory shear flow at the single frequency of 0.1 rad/s for 2 h, and (c) the edge of POE(D15) subjected to small-amplitude oscillatory shear flow at the single frequency of 0.1 rad/s for 2 h.

diffusion of oxygen or the chemical reaction between the oxygen and macroradicals. For a cyclic sample, the viscosity increase could be attributed to oxidation crosslinking in the outer ring or in the internal circle; this depends on the different kinetics. The relation between the diffusion rate and reaction rate can be analyzed as follows.

The thermal oxidation process of POE involves free-radical-initiated chain reactions and proceeds in three basic steps: initiation, propagation, and termination.²¹ Depending on the results of rheological measurements, FTIR analysis, and gel content measurements, reactions leading to polymer crosslinking dominate the termination step.

The correlation of the diffusion of oxygen and the chemical reaction can be expressed as follows:

$$\frac{\partial c_{O_2}(r, t)}{\partial t} = D_{O_2} \nabla^2 c_{O_2}(r, t) - k c_{O_2}(r, t) \quad (1)$$

where c_{O_2} is the concentration of oxygen in POE, D_{O_2} is the diffusion coefficient of oxygen in POE, k is the rate constant, and a first-order reaction is assumed.

TABLE II
Gel Contents of Samples Subjected to a Small-Amplitude Oscillatory Shear Flow in the Linear Viscoelastic Regime at a Strain of 5% and a Single Frequency of 0.1 rad/s for 2 h

Sample	Virgin mass (g)	Gel mass (g)	Gel content (%)
POE(Pure)	0.3557	0.0161	4.53
POE(Antioxidant)	0.3193	0	0

TABLE III
Critical Times at Which η^* Rises Sharply

Sample	POE (Antioxidant)	POE (D5)	POE (D15)	POE (D20)
Diffusion time (s)	102,796	65,789	16,447	4,112
Exhaustion time (s)	2,834	2,720	1,813	1,020
Experimental time (s)	2,834	2,406	1,827	1,008

When the diffusion of oxygen into POE is in a steady state, c_{O_2} can be extracted from eq. (1) in cylindrical coordinates:

$$c_{O_2}(r) = c_0 I_0\left(\sqrt{kR^2/D_{O_2}} \frac{r}{R}\right) / I_0\left(\sqrt{kR^2/D_{O_2}}\right) \quad (2)$$

where $I_0(x)$ is the first kind of Bessel function and oxygen diffuses from edge $r = R$ into POE. When $kR^2/D_{O_2} \gg 1$, the front of diffusing oxygen correlates with $\sqrt{D_{O_2}/kR^2}$. For cyclic samples, if the diffusing distance of the oxygen front is larger than the width of the outer ring, the oxidation is attributed to the inside part of the samples. Otherwise, the oxidation starts only at the edge of the whole samples, and the rate of the oxidation depends on the concentration of the antioxidant.

If the consumption of oxygen is neglected, the maximum distance that oxygen can diffuse in a polymer melt can be estimated by $\Delta X^2 = 2D_{O_2}t$, where ΔX is the distance and t is the experimental time. The diffusion coefficient of oxygen can be estimated as $7.6 \times 10^{-10} \text{ m}^2/\text{s}$.²² Therefore, we can calculate the critical time (the diffusion time) at which the reaction starts if the thermal oxidation of POE is controlled by the diffusion of oxygen. The results are listed in Table III. However, the diffusion of oxygen is much slower. The diffusion time is much longer than the experimental time at which thermal oxidation happens. Therefore, it is impossible for oxygen to penetrate the cyclic layer with the antioxidant, and this means that all the reactions should take place in the outer cyclic layer.

Because $kR^2/D_{O_2} \gg 1$ (corresponding to the very limited thickness of the oxygen layer) and the antioxidant takes part in the reaction only when the diffusion coefficient of the antioxidant in POE is comparable to D_{O_2} , the polymer propagating radicals ($ROO\cdot$) can be removed. Actually, the diffusion coefficient of the antioxidant in polyolefins at 220°C is about $7.0 \times 10^{-10} \text{ m}^2/\text{s}$,²³ which is quite comparable to the diffusion coefficient of oxygen. Therefore, the results imply that the thermal oxidation of the cyclic samples starts at the edge of the samples and is controlled by the concentration of the antioxidant. The exhaustion time of the antioxidant of cyclic samples can be evaluated from the rheological measurements.

POE(Antioxidant) was subjected to a small-amplitude oscillatory shear flow at the single frequency of 0.1 rad/s while η^* was monitored with time. Figure 5 shows that η^* of POE with the antioxidant is almost constant until an increase at 2834 s. Assuming that the oxidant of POE(Antioxidant) is exhausted in 2834 s, the mass of the antioxidant in the cyclic samples can be calculated by $(\pi/4)(D_0^2 - D_v^2)h\rho w$, where D_v is the diameter of the virgin POE, D_0 is the diameter of the whole cyclic sample, D denotes the diameter of the round disk, h denotes the thickness of the round disk, ρ denotes the density of the polymer, and w is the weight fraction of the antioxidant. The exhaustion time of the antioxidant in POE(D20), POE(D15), and POE(D5) can be estimated from the exhaustion time of the antioxidant in POE(Antioxidant) as follows:

$$t_{ex} = t_0 \frac{D_0^2 - D_v^2}{D_0^2} \quad (3)$$

where t_{ex} is the exhaustion time and t_0 is the critical time when the complex viscosity of POE(Antioxidant) increases sharply. The exhaustion time of the antioxidant is quite close to the start time of the viscosity increase. The whole process can be described as follows: when the oxygen diffuses into the sample at $r = R$, it reacts with macroradicals quickly, and this results in a thin layer of oxygen due to $kR^2/D_{O_2} \gg 1$. On the other hand, the antioxidant in the thin oxygen layer is consumed by a reaction with $ROO\cdot$. The consumed antioxidant is supplied by the diffusion. The consumption of the oxygen and antioxidant is a dynamic balance due to comparable diffusion coefficients in the melt. Further oxidation reactions happen when the antioxidant is consumed completely.

CONCLUSIONS

We have studied the thermal oxidation of metallocene-catalyzed POE by a rheological method. It is sensitive for detecting the thermal oxidation of POE. The results show that the thermal-oxidation-induced crosslinking reaction occurs in the POE melt at a high temperature. The amount of the antioxidant determines the thermal oxidation of POE when the antioxidant is added, and the diffusion of oxygen controls the thermal oxidation of POE without the antioxidant. In addition, FTIR and gel content characterization confirms that crosslinking occurs and that carbonyl groups form in the reaction.

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