

Methodology for Development of New Active Barrier PET Copolymers

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ABSTRACT: Active barrier developments for poly(ethylene terephthalate) (PET) are among important approaches being used to achieve improvements in the polyester's barrier properties. This work utilized two active barrier materials and their PET copolymers, synthesized by melt polymerization of terephthalic acid (TPA) with ethylene glycol (EG) and active oxygen scavengers: monoolein (MO) or 3-cyclohexene-1,1-dimethanol (CHEDM), in separate compositions. The oxidizable monomers and their copolymers were characterized with respect to changes resulting from their reactions with oxygen. Evaluations of their infrared and nuclear magnetic resonance spectra established that the monomers as well as their PET copolymers underwent first order reactions and had rate constants ranging from 0.03 to 0.08 day⁻¹. The only volatile oxidation product of MO was acetaldehyde and no volatile products resulted from oxidation of CHEDM. In comparison to unmodified PET, the PET/MO and PET/CHEDM copolymers achieved respective oxygen barrier property improvements of about 30 and 40%. Results from this study have shown that the oxidation kinetics of pure monomers of this type may be used for evaluation of their effectiveness and suitability as active barrier materials, without the need to synthesize their corresponding PET copolymers. This is significant and work is continuing to include other moieties that will interact with higher levels of oxygen and react at faster rates. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 4273–4283, 2013

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INTRODUCTION

The need for poly(ethylene terephthalate) (PET) with improved oxygen barrier properties has been previously discussed.¹ Technologies for improving barrier performance include coatings, blends of barrier materials with existing polymers, nanocomposite materials, and new active barrier polymers.² Some of these technologies are commercially available, while others are under development.

The presence of an active barrier scavenger in a PET container's polymer matrix is expected to delay oxygen transmission until after complete reaction of the scavenger. Oxygen transmission would then achieve a steady state, similar to that observed for unmodified PET. The Oxbar[®] active barrier system is said to provide a total barrier to oxygen ingress for as long as the reactants are present. It is reported that a 1-l PET bottle has an oxygen transmission value of 3.5 cc m⁻² day⁻¹ at room temperature; while an equivalent Oxbar[®] (PET/4%MXD6/cobalt blend) bottle has a value of less than 0.04 cc m⁻² day⁻¹.³ Amosorb[®] technology is another commercially available active barrier that includes polybutadiene segments copolymerized with PET, at loadings of 4 to 12 wt %, to provide significant improvements in its oxygen barrier properties.⁴ In this PET copolymer

the polybutadiene segments tend to aggregate into more organized olefin-rich domains that can reduce polymer clarity.

If PET is modified with an oxygen scavenger in its main chain, reactions with oxygen can result in chain scissions that produce low molecular weight products. In the case of blends of MXD6 and PET, this can occur as amide sites are attacked along the polymer chain. Another disadvantage of MXD6 and PET blends is that they generally have poor clarity after being stretched, as a result of anisotropic differences in their refractive indices.^{5, 6}

These problems can be overcome if PET is copolymerized with active oxygen scavengers having oxidizable pendant side groups. When oxygen reacts with these pendant groups, there will be no chain scission of the main PET chain and packaged materials will not be exposed to oxidation byproducts. As previously described¹ oxygen scavengers used in this research were monoolein (MO) (C₂₁H₄₀O₄), which is a branched diol with mono-unsaturation in its side chain and 3-cyclohexene-1,1-dimethanol (CHEDM) (C₈H₁₄O₂), which is a branched diol with cycloalkene unsaturation in its side chain. The previous article¹ also described synthesis of the PET/scavenger copolymers as well as effects of the oxygen scavengers on rheological and thermal properties.

The current article discusses methodologies developed for determining oxygen scavenging capacity and scavenger kinetics, as well as the effects of oxygen scavengers on the oxygen barrier properties of PET. The formation of oxidation by-products was investigated and a process was developed to determine the effectiveness or oxygen scavenging capacity of the additives. This study will enable researchers to quickly evaluate and predict the applicability of potential oxygen scavengers in terms of their ability to scavenge oxygen efficiently, before synthesis of their PET copolymers.

EXPERIMENTAL

Materials

Cobalt octoate was provided by Shepherd Chemicals (Norwood, OH). All other materials [terephthalic acid (TPA), ethylene glycol (EG), MO, CHEDM, etc.], used in this research, have been discussed previously.¹

Processing and Characterization

In situ polymerization reactions were performed in a batch scale melt polymerization system described previously.¹

A laboratory scale Brabender single screw extruder was used to prepare extruded PET and PET/scavenger copolymer sheet samples suitable for oxygen permeability measurements. All the resins were vacuum dried overnight at 130°C before extrusion, and extruded with all zones held at 270°C and a screw speed of 80 rpm. Emerging extrudate was processed through a set of chilled squeeze rolls to prepare sheet samples about 0.1–0.2 mm thick.

Cobalt catalyst in the form of cobalt octoate was added to portions of the PET/scavenger (5 wt %) copolymers before processing. This catalyst was expected to enhance the uptake of oxygen,^{7, 8} reduce the activation energy of the oxidation reaction between the scavenger and oxygen, and allow the reaction to occur at room temperature.

Oxygen permeability was determined by measuring the oxygen transmission rate (OTR) at steady state using a whole package MoCon (Minneapolis, MN) tester according to ASTM D3985 described previously.¹

The densities of the PET/scavenger copolymers were calculated by determining their specific gravities and corresponding densities according to ASTM D792-98.

Viscosity of MO was measured using ASTM D 1545-89, bubble time method.

The apparatus used to experimentally determine the oxygen scavenging capacity of the MO scavenger included a pressure gauge connected with a small cylindrical metal chamber containing the scavenger and oxygen. This apparatus utilized the concept that known numbers of moles of oxygen and scavenger could be placed inside the sealed system. Initially, an excess number of moles of oxygen were placed in the chamber in comparison to the number of moles of scavenger. This was done in order that an equilibrium condition, with respect to moles of oxygen, could be achieved when the entire scavenger was consumed over the experimental time. Measurements were performed in duplicate.

A Perkin Elmer (Waltham, MA) 1600 series Fourier transform infrared spectroscopy (FTIR) instrument was used to study the oxidation kinetics of pure scavenger. A very thin layer of MO was spread on a potassium bromide disc and oxidized for various times at 50°C in a circulating air oven. Sixty-four scans (from 400 to 4000 cm⁻¹) were performed for each determination. Samples were examined in the transmission mode, with an instrument resolution of 4 cm⁻¹. Peak height absorbance values were determined using standard Perkin Elmer software.

Solution proton nuclear magnetic resonance spectroscopy (¹H NMR) was used to study the oxidation of the scavengers and copolymers. A 70/30 (wt/wt) *d*-chloroform/trifluoro acetic acid (TFA) mixture was used to dissolve the scavengers and ground copolymer samples. Measurements were performed in a high resolution INOVA-600 MHz spectrometer manufactured by Varian Association Inc. (Palo Alto, CA). For measurements of the oxidation of pure MO, 16 scans were recorded. In the case of oxidation measurements of CHEDM and the copolymer samples, 64 scans were recorded for better resolution of smaller peaks.

During the oxidation of PET/scavenger copolymers and pure scavengers, small molecules of oxidation product could be released into the atmosphere. Gas chromatography-mass spectrometry (GC-MS) was used to determine if this had occurred and to identify any oxidation products. Measurements were performed with a Hewlett-Packard (Palo Alto, CA) HP-G1800B GCD coupled to a mass detector operated in the electron ionization (EI) mode. The EI spectra were obtained over the range *m/z* = 10–200 using an Agilent Technologies HP-1 column at a column temperature of 83°C.

Two of the sample vials contained pure air and MO in air. The other three vials contained CHEDM and finely ground copolymers of PET/MO and PET/CHEDM in air, to which, additional oxygen had been added to provide an oxygen rich environment for reaction. All vials were placed in an oven at 50°C. After 12 days of oxidation, 5 µL of headspace gas was removed from each sealed vial and injected into the GC-MS to obtain degradation spectra. The spectrum of pure air was used as a reference.

A vial containing pure MO scavenger and air was further analyzed to determine the specific nature of any oxidation products that could be released into the atmosphere. Gas chromatography (GC) headspace measurements were performed with a Perkin-Elmer TurboMatrix 40 headspace sampler paired with an AutoSystem XL gas chromatograph (GC). The helium purged GC utilized a 30 m by 0.32 mm ID Stabilwax®-DA column maintained at 60°C and a flame ionization detector.

RESULTS AND DISCUSSION

Oxygen Scavenging Capacity

The theoretical oxygen scavenging capacity of each scavenger additive was calculated by assuming that each of its molecules had one double bond, with which one oxygen molecule could react. For a PET copolymer containing 5% MO, relative concentrations included 1.462 mol of EG, 0.038 mol of MO, and 1 mol of TPA, maintaining a constant total molar concentration for the EG plus comonomer of 1.5 : 1 mol TPA. One mole of MO

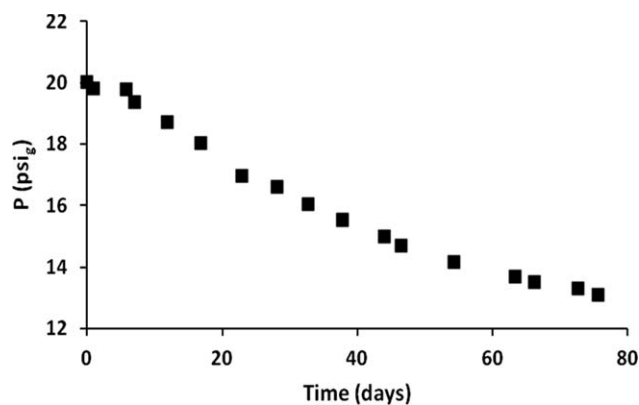


Figure 1. Oxygen pressure plotted as a function of storage time in the presence of MO.

contains 6.02×10^{23} molecules; therefore 0.038 mol contain 2.29×10^{22} molecules, indicating that this copolymer can absorb 2.29×10^{22} molecules of oxygen. From the ideal gas law,

$$PV = nRT \quad (1)$$

where at STP conditions, P is the pressure of oxygen, V the volume of oxygen that can be absorbed, n the number of moles of oxygen, R the gas constant, and T the temperature. In this case, $V = 862.5 \text{ cm}^3$. From this, the ratio of oxygen volume to grams of PET/MO copolymer and to grams of scavenger can be calculated to obtain values of $3.2 \text{ cm}^3 \text{ oxygen g}^{-1}$ PET/MO copolymer and $63.6 \text{ cm}^3 \text{ oxygen g}^{-1}$ MO.

For a PET copolymer containing 5% CHEDM, relative concentrations include 1.405 mol of EG, 0.095 mol of CHEDM, and 1 mol of TPA. Calculations similar to those applied for MO were performed for CHEDM. Theoretical values for volumes of oxygen, able to be reacted were $8.1 \text{ cm}^3 \text{ oxygen g}^{-1}$ PET/CHEDM copolymer and $159.1 \text{ cm}^3 \text{ oxygen g}^{-1}$ CHEDM.

An experimental technique was developed for measurement of oxygen scavenging capacity. It utilized a sensitive pressure gauge within an inert sealed system containing MO scavenger and oxygen under known pressure. Figure 1 shows an example of measured oxygen pressure, plotted as a function of storage time in the presence of MO. The pressure decreased, as oxygen reacted with the scavenger, and eventually attained an equilibrium value. Through STP ideal gas law conversions of initial and final pressures, the experimental volume of oxygen consumed was found to be $52.3 \text{ cm}^3 \text{ g}^{-1}$ of MO scavenger. The scavenger capacity is thus 2.3×10^{-3} mol of oxygen consumed per g MO scavenger. If one gram of MO constitutes 0.0028 mol then the ratio of molecules of oxygen consumed to molecules of MO is equal to 0.81. This experimental result validates the previous assumption that one double bond of one scavenger molecule will react with one oxygen molecule.

Oxidation Kinetics of MO and PET/MO Copolymer

FTIR spectroscopy was used to determine the oxidation kinetics of pure MO scavenger by following reductions in unsaturated double bonds as functions of oxygen exposure times at 50°C . Figure 2(a) shows the structure of pure MO with spectra given in Figure 2(b)–(d). It can be seen that height of the peak at 3010

cm^{-1} decreases with exposure time. This IR band corresponds to *cis*-C=C–H symmetric stretching.^{9,10} Oxidation of MO occurs through a free radical mechanism that includes the formation of hydroperoxides that decompose, yielding oxidation products such as alcohols, aldehydes, or ketones.¹⁰ The peak at 1170 cm^{-1} corresponds to an ester vibration (–C(O)–OCH₂–)^{8,9} that does not change as a result of oxidation. It was, therefore, taken as an internal reference. Table I lists heights of the peaks at 3010 and 1170 cm^{-1} after various times of oxidation. As a result of scavenger oxidation, decrease in the *cis*-C=C–H planar bending peak^{8,9} at 723 cm^{-1} can also be observed in Figure 2(b) and (d).

Changes in the normalized $[H(3010 \text{ cm}^{-1})/H_1(1170 \text{ cm}^{-1})]$ MO absorbance peak heights (R), as a function of exposure times were used to determine oxidation kinetic parameters through integral and differential methods; as well as Polymath nonlinear regression analysis. According to the integral method, a plot of $\ln(R/R(t_0))$ versus time was constructed. If it is assumed that oxygen is in excess and the reaction is first-order, it can be described according to eq. (2).

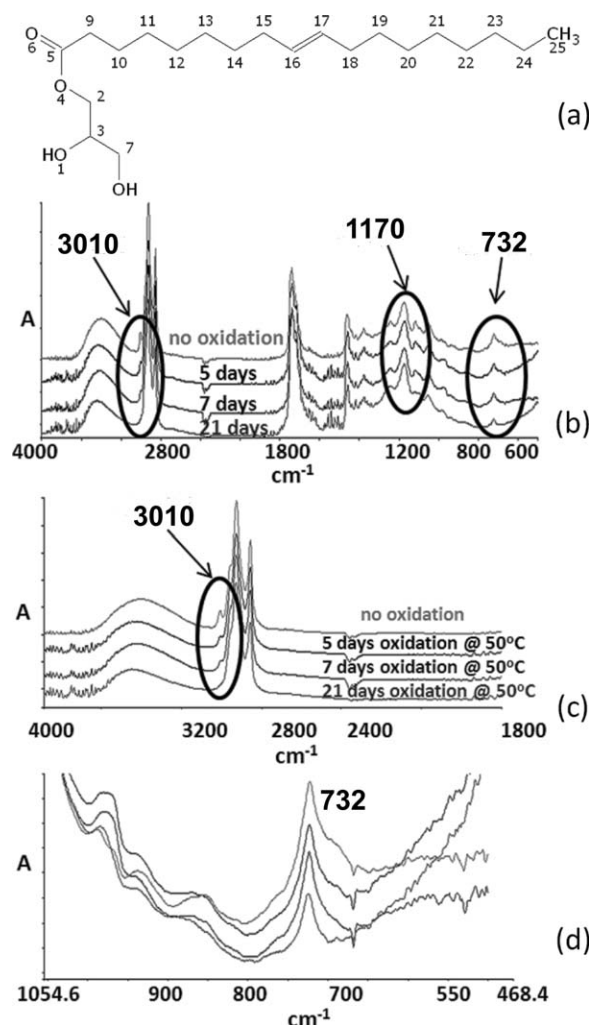


Figure 2. (a) Structure of pure MO, (b) FTIR spectra of pure MO before and after oxidation at 50°C , (c) and (d) expansion of selected regions of the FTIR spectra shown in (b).

Table I. FTIR Absorbance Peak Heights and Calculated Ratios for Pure MO, After Various Oxidation Storage Times at 50°C

Time (days)	Height of 3010 cm ⁻¹ peak (H)	Height of 1170 cm ⁻¹ reference peak (H ₁)	Normalized peak height (R = H/H ₁ = C _A)	ln(R/R(t ₀))
0	0.0314	0.0569	0.55	0
1	0.0279	0.0552	0.51	-0.076
2	0.0266	0.0589	0.45	-0.201
4	0.0235	0.0595	0.39	-0.344
7	0.0185	0.0567	0.33	-0.511
11	0.0171	0.0586	0.29	-0.640
13	0.0146	0.0592	0.25	-0.789
15	0.0132	0.0588	0.22	-0.916
18	0.0105	0.0584	0.18	-1.117
21	0.0094	0.0587	0.16	-1.235

$$-dC_A/dt = kC_A \quad (2)$$

As shown in Figure 3(a), data in the plot of $\ln(R/R(t_0))$ versus time fits to a linear region indicating that the reaction is pseudo-first order and the slope is equal to the rate constant of oxidation (k). The slope is $-k$ (-0.062), thus k is 0.062 day^{-1} .

According to the differential method,

$$A(\text{MO}) + B(\text{O}_2)_{\text{Excess}} = \text{products} \quad (3)$$

For an irreversible reaction, the rate law can be written as shown in eq. (4).

$$-r_A = kC_A^a C_B^b \quad (4)$$

Here r_A is the rate, C_A and C_B are MO and O₂ concentrations, and superscripts "a" and "b" are their respective reaction orders. Using method of excess,

$$\ln(-dC_A/dt) = \ln(-\text{rate}) = \ln(k) + a \ln(C_A) \quad (5)$$

The slope of a plot of $\ln(-dC_A/dt)$ versus $\ln(C_A)$ is the reaction order. To obtain the derivative ($-dC_A/dt$) used in this plot, the concentration–time data must be differentiated by fitting the concentration–time data to a second order polynomial [according to eq. (6)] as shown in Figure 3(b).

$$C_A = a_0 + a_1 t + a_2 t^2 \quad (6)$$

Here, the a_i 's are the constants.

$$dC_A/dt = a_1 + 2a_2 t \quad (7)$$

The reaction order and rate constant can now be found from a plot of $\ln(-dC_A/dt)$ versus $\ln(C_A)$, as shown in Figure 3(c). From this figure, the slope is 1.2, the intercept is $\ln(k)$ (-2.61), and k is 0.074 day^{-1} .

Polymath software uses nonlinear regression to determine the set of kinetic parameters for which the model will best fit a set of experimental data. This software was used to determine the kinetic parameter values (α , k) for which the sum of the squares of the differences, of the measured parameter and the calculated

parameter is a minimum.¹¹ For concentration–time data, the measured parameter has a concentration (C_A). The mole balance equation and rate law can be integrated, when dC_A/dt is $-C_A^\alpha$, to obtain:

$$C_A = [C_{A0}^{1-\alpha} - (1-\alpha)kt]^{1/1-\alpha} \quad (8)$$

By rearranging this equation, we obtain:

$$t = (C_{A0}^{1-\alpha} - C_A^{1-\alpha}) / k(1-\alpha) \quad (9)$$

According to regression analysis, the variable C_{A0} is 0.53, the order (α) is 1.29, and k is 0.082.

Comparisons of the orders of reaction and rate constant (k) values, calculated with the three methods from FTIR data for pure monoolein, are given in Table II. These values are very similar (with good R^2 values), confirming that the oxidation reaction order for pure MO is 1 with rate constant values between 0.06 – 0.08 day^{-1} .

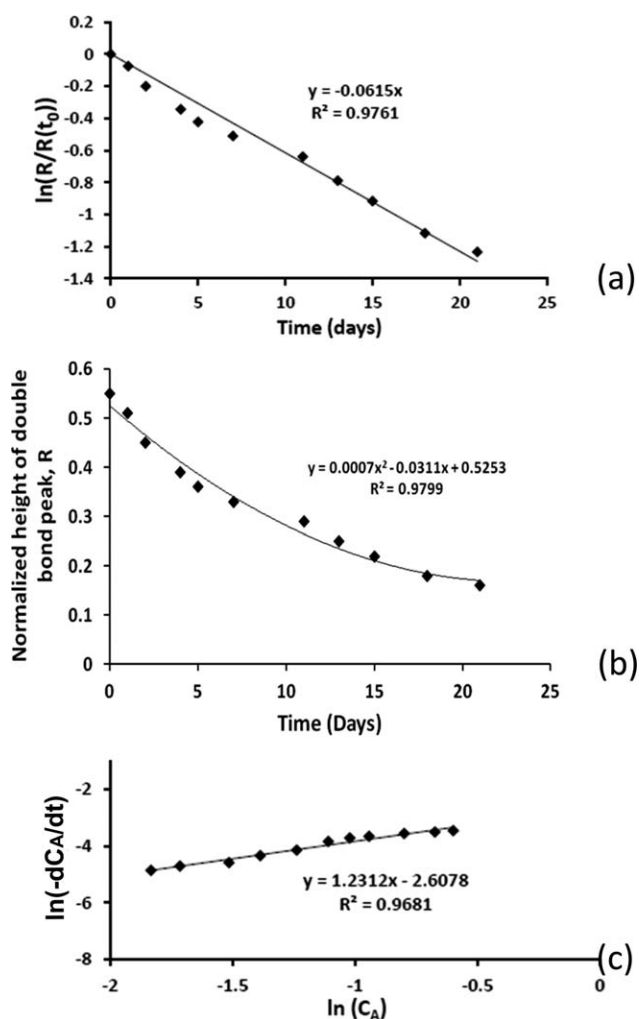


Figure 3. Oxidation kinetic parameters for pure MO using: (a) an integral method to obtain a plot of $\ln(R/R(t_0))$ as a function of exposure time and (b) a differential method to obtain a plot of normalized height of peak at 3010 cm^{-1} as a function of exposure time, and (c) a plot of $\ln(-dC_A/dt)$ as a function of $\ln(C_A)$.

Table II. Order of Reaction and k Values for Pure MO Oxidized at 50°C, from FTIR Data

Parameter	Integral method	Differential method	Polymath
Order (α)	1.0	1.2	1.3
Rate constant (k), day ⁻¹	0.062	0.074	0.080
R ² value	0.98	0.97	0.99

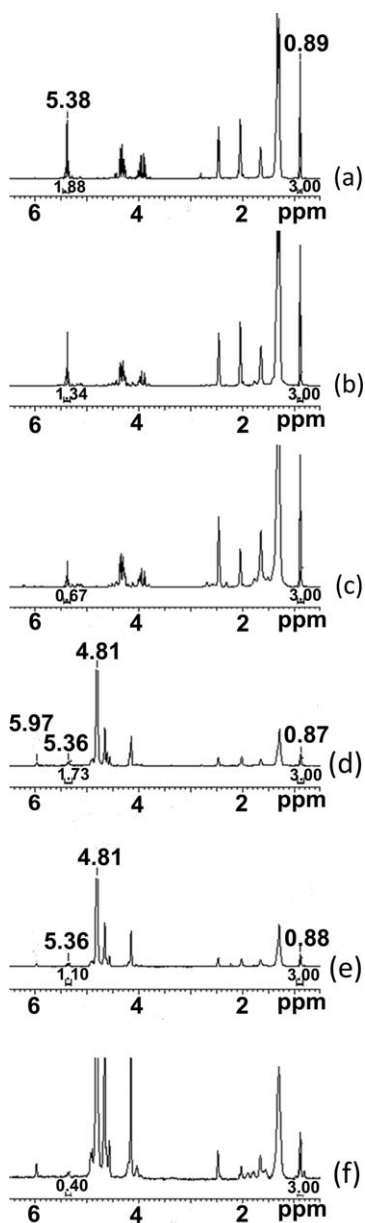


Figure 4. Oxidation reaction analysis at 50°C with ¹H NMR spectra of pure MO (a) before oxidation), (b) oxidized for 8 days, and (c) oxidized for 21 days. Similar analysis of PET/MO copolymers (d) before oxidation), (e) oxidized for 15 days, and (f) oxidized for 39 days.

Table III. Peak Areas and Ratios After Various Oxidation Storage Times at 50°C for Pure MO and PET/MO Copolymer, from NMR Data

Time (days)	Area under double bond peak (A)	A(t0)	ln(A/A(t0))
<i>Pure MO</i>			
0	1.88		0
8	1.34		-0.34
14	1.02	1.88	-0.61
21	0.67		-1.03
35	0.36		-1.65
<i>PET/MO copolymer</i>			
0	1.73		0
7	1.41		-0.20
15	1.10	1.73	-0.45
24	0.76		-0.82
39	0.40		-1.46

Oxidation kinetics of pure MO was also studied with ¹H NMR spectroscopy. For these evaluations, samples were prepared by oxidizing pure MO, placed in aluminum pans and held at 50°C for 35 days in a circulating air oven. Figure 4(a) shows the ¹H NMR spectrum for an unoxidized sample of pure MO, while Figures 4(b) and (c) illustrate its spectra after 8 and 21 days of exposure. In the case of MO before oxidation, the peak of protons of -CH=CH- at $\delta = 5.38$ ppm has an area of 1.88. Equivalent samples oxidized for 8 and 21 days, have respective areas of 1.34 and 0.67.

The numbers of protons representing unsaturated double bonds decreased after oxidation. Areas under peaks of the -CH₂- protons of -CH₂-CH=CH-CH₂- of the monoolein unit at $\delta = 2.04$ ppm also decreased after oxidation, because of the changes in the chemical environment around the double bond as a result of oxidation. The upper part of Table III gives examples of the area data recorded for the double bond peak (A) as a function of exposure time for pure MO oxidized at 50°C. These areas are normalized with respect to the -CH₃ group peak, which does not change as a result of the oxidation reaction.

Table IV. Order of Reaction and Rate Constant (k) Values for Pure MO and PET/MO Copolymer Oxidized at 50°C, from NMR Data

Parameter	Integral method	Differential method	Polymath
<i>Pure MO</i>			
Order (α)	1.0	1.1	1.0
Rate constant (k) (day ⁻¹)	0.050	0.044	0.050
R ² value	1.00	0.93	1.00
<i>PET/MO copolymer</i>			
Order (α)	1.0	0.7	0.6
Rate constant (k) (day ⁻¹)	0.036	0.034	0.036
R ² value	0.99	0.99	1.00

Table V. Rate Constant (k) and Activation Energy (E_a) Values, Calculated from NMR Data, for PET/MO Copolymer Oxidized at Various Temperatures

Temperature (°C) K	1/T (K)	k (day ⁻¹)	ln(k)	E_a kJ/mol (kcal/mol)
(70) 343	0.002915	0.081	-2.51	
(60) 333	0.003003	0.053	-2.94	37 (8.9)
(50) 323	0.003096	0.036	-3.32	
(25) 298	0.003356	0.011 ^a	-4.50 ^a	-

^aExtrapolated value

As with the FTIR evaluations, oxidation kinetic parameters were determined for pure MO from the data collected from ¹H NMR spectroscopy. These determinations also utilized integral and differential methods as well as Polymath nonlinear regression analysis. Table IV gives the order of reaction and rate constant (k) values calculated by the three methods. These values are all very similar (with good R^2 values) confirming that the order of the oxidation reaction for pure MO is 1 and the rate constant varies between 0.04–0.05 day⁻¹.

The rate constants of oxidation (k) for pure MO calculated using the FTIR data (Table II) and the NMR data (Table IV) are slightly different. Variations in k values could result from differences in the FTIR and NMR techniques and methods used to calculate the k values, in addition to differences in sample conditions during oxygen exposure and treatment of the samples during analysis. Effects of oxygen diffusion, through different sample thicknesses during evaluations by the two methods could be another possible cause for the variations. To investigate this possibility, a correlation for liquid diffusivity (D_v) of small molecules was used. These calculations employed the empirical Wilke–Chang equation¹² given below.

$$D_v = 7.4 \times 10^{-8} (\psi_B M_B)^{1/2} T / \mu V_A^{0.6} \quad (10)$$

For pure monoolein the association parameter (ψ_B) is 1, the molecular weight (M_B) is 356.55 g mol⁻¹, temperature (T) is 298 K, molar volume (V_A) is 25.6 cm³ mol⁻¹,¹³ and viscosity (μ) is 215 cP. From eq. (10), $D_v = 2.77 \times 10^{-7}$ cm² s⁻¹. As an example, the time (t) required for oxygen to diffuse through

85% of the thickness of a 3 mm slab of MO can be calculated according to eq. (11).¹³

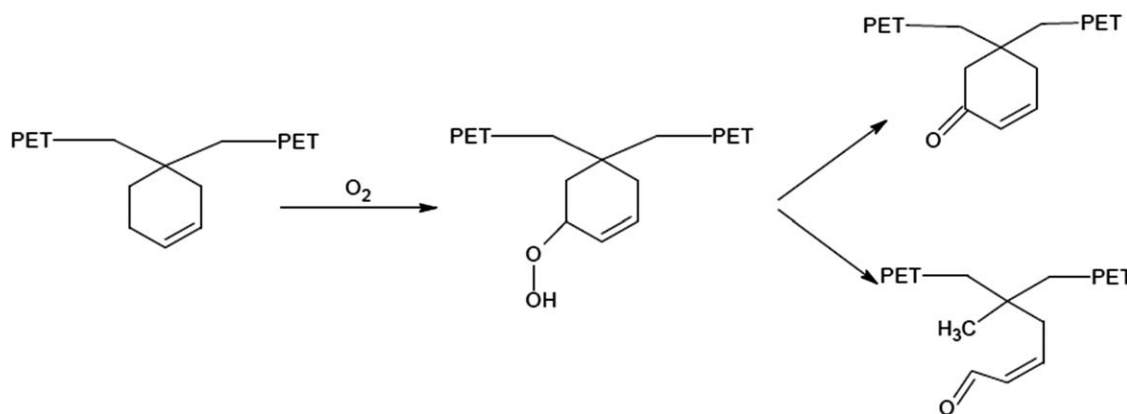
$$D_v \times t / L^2 = 0.68 \quad (11)$$

Here, L is the half thickness of the sample and t is 0.64 day. This time is very short; therefore, it appears that diffusion does not have a significant effect on the observed k values.

Oxidation kinetics of PET/MO copolymer samples were studied using NMR data in a manner similar to that described for the pure MO. The finely ground copolymer samples were prepared for ¹H NMR spectroscopy by exposing them to air at 50°C for 39 days. Use of the finely ground samples reduced the effects of diffusion through a thicker polymer film and also enabled them to be more easily dissolved for analysis without additional processing after oxidation. Figure 4(d) shows the ¹H NMR spectrum of PET/MO (5 wt %) copolymer before oxidation, while Figure 4(e) and (f) give spectra for oxidized samples of the copolymer. Before oxidation, the peak representing protons of –CH=CH– at $\delta = 5.36$ ppm, had an area of 1.73; while the peak of a sample oxidized at 50°C for 15 days, had an area of 1.10 [Figure 4(e)] and that for a sample oxidized for 39 days an area of 0.40 [Figure 4(f)]. These results indicate that the numbers of double bond protons are decreasing as a result of oxidation of the monoolein part of the copolymer. Table III gives examples of the normalized (with respect to the –CH₃ group peak) area data, recorded after various copolymer oxidation exposure times at 50°C.

The oxidation kinetic parameters of PET/MO copolymer were determined from the NMR data, as with the pure MO. Table IV gives the order of reaction and rate constant (k) values calculated by the three previously described methods. These values are very similar, confirming that the order of the oxidation reaction for PET/MO copolymer sample is 1 and the rate constant between 0.034–0.036 day⁻¹. It should be noted that values given on Table IV for pure MO and for PET/MO copolymer are very similar; indicating that results obtained for the pure scavenger can be used to predict scavenger copolymer behavior.

Rate constant values for the oxidation reaction of PET/MO copolymer samples were also determined in the same manner at 60 and 70°C. With the Arrhenius equation, these results were then used to calculate an activation energy (E_a) of 37 kJ mol⁻¹

**Figure 5.** Proposed mechanism for oxidation of CHEDM (with ring opening, but not dissociation from polymer backbone).

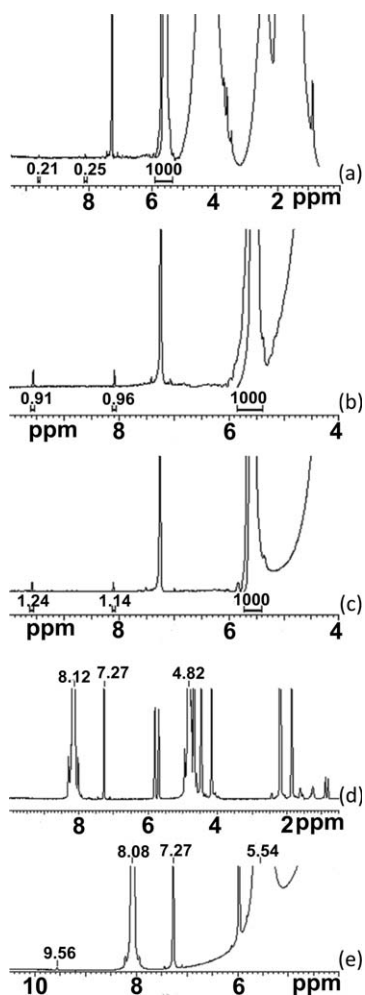


Figure 6. Oxidation reaction analysis at 50°C with ^1H NMR spectra of pure CHEDM oxidized for (a) 4 days, (b) 14 days, and (c) 19 days. Similar analysis of PET/CHEDM copolymers oxidized for (d) 7 days without catalyst and (e) 9 days with catalyst.

(8.9 kcal mol $^{-1}$) and a pre-exponential factor of 10.6. At 25°C (298 K) extrapolation of the plot gave a rate (k) of 0.011 day $^{-1}$. Table V gives the extrapolated rate constant and $\ln(k)$ value as well as those determined from NMR data obtained at oxidation temperatures of 323, 333, and 343 K. It should be noted that the only changes observed in the PET/MO spectra were similar to those observed for the pure MO monomer, in the absence of PET. No significant changes were seen in the “PET” portions of the spectra.

Oxidation Kinetics of CHEDM and PET/CHEDM Copolymer

An oxidation mechanism proposed for the CHEDM copolymer is illustrated in Figure 5. It can be seen that oxidation may lead to the formation of ketones or aldehydes, whose ^1H NMR peaks would appear between $\delta = 9.5$ –10.0 ppm. By following changes in this peak, ^1H NMR spectroscopy was used to characterize the oxidation kinetics of the pure CHEDM and the PET/CHEDM copolymer samples prepared by oxidation at 50°C. Figure 6(a) shows a spectrum of CHEDM oxidized for 4 days in the presence of cobalt catalyst. The peak representing oxidation byproduct protons at $\delta = 9.6$ ppm has an area of 0.21. In the case of

Table VI. Peak Areas and Ratios After Various Oxidation Storage Times at 50°C for Pure CHEDM and PET/CHEDM Copolymer, from NMR Data

Time (days)	Relative area under oxidation byproduct peak (C_P/C_A)	C_{AO}	$C_A = C_{AO}/(1 + C_P/C_A)$	$\ln(C_A/C_{AO})$
<i>Pure CHEDM</i>				
0	0		2.00	0
4	0.21		1.65	-0.19
7	0.51	2.0	1.32	-0.42
10	0.66		1.20	-0.51
14	0.91		1.05	-0.64
19	1.24		0.89	-0.81
<i>PET/CHEDM copolymer</i>				
0	0		2.00	0
5	0.19		1.68	-0.17
9	0.50	2.0	1.33	-0.41
11	0.65		1.21	-0.50
16	0.88		1.06	-0.63

CHEDM oxidized for 14 and 19 days [Figure 6(b,c)], areas increased to 0.91 and 1.24, indicating increased numbers of oxidation byproduct protons. Table VI gives additional oxidation data.

The oxidation kinetic parameters of CHEDM were determined from the NMR data with the previously described integral and differential methods. Table VII indicates that the orders of reaction and rate constants (k) calculated by the two methods are very similar and have good R^2 values. This confirms that the order of the oxidation reaction for pure CHEDM is 1 with a rate constant between 0.033–0.046 day $^{-1}$.

The oxidation reaction of PET/CHEDM copolymer was also studied using ^1H NMR spectroscopy for evaluation of finely ground samples oxidized at 50°C. Figure 6(d) shows that after oxygen exposure for 7 days at 50°C, a PET/CHEDM copolymer sample prepared without catalyst, has no peak representing

Table VII. Order of Reaction and Rate Constant (k) Values for Pure CHEDM and PET/CHEDM Copolymer Oxidized at 50°C, from NMR Data

Parameter	Integral method	Differential method
<i>Pure CHEDM</i>		
Order (α)	1	0.9
Rate constant (k) (day $^{-1}$)	0.046	0.033
R^2 value	0.96	0.93
<i>PET/CHEDM copolymer</i>		
Order (α)	1	-
Rate constant (k) (day $^{-1}$)	0.041	-
R^2 value	0.98	-

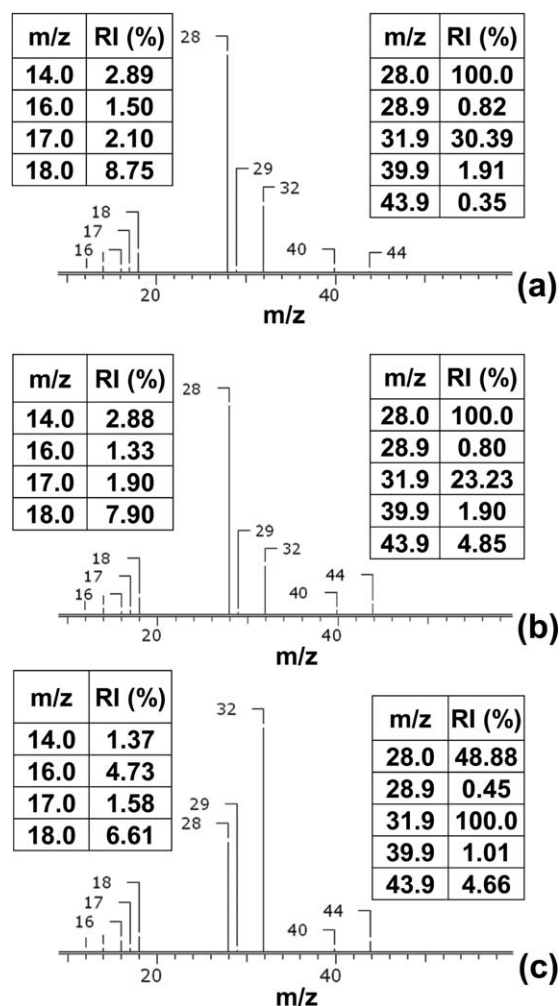


Figure 7. GC-MS spectra of (a) pure Air, (b) pure Monoolein, and (c) PET/MO copolymer.

protons of the oxidation byproduct at $\delta = 9.56$ ppm. Figure 6(e) gives an example of spectra obtained for PET/CHEDM copolymer prepared with 400 ppm catalyst and oxidized at 50°C for 9 days. Table VI gives similar results obtained for the other catalyst containing samples. Table VII gives the calculated order of reaction and rate constant (k) values determined with the Integral method, indicating that the order of the oxidation reaction for the PET/CHEDM copolymer is 1 and the rate constant value is 0.041 day^{-1} . As with the MO and PET/MO copolymer; these copolymer values are very similar to those obtained for the pure CHEDM and no significant changes were observed in the “PET” portions of the spectra.

Oxidation By-Products of Scavengers and PET/Scavenger Copolymers

During the oxidation of PET/scavenger copolymers, small oxidation product molecules could be released into the atmosphere or inside the package to the product. Gas chromatography-mass spectrometry (GC-MS) was used to identify any volatile oxidation byproducts. Five vials respectively containing air, and portions of MO, CHEDM, PET/MO copolymer, and PET/CHEDM copolymer in air were held at 50°C. After 12 days of oxidation,

gas specimens from each vial were injected into the GC-MS. The spectrum of pure air, shown in Figure 7(a), was used as reference. In this figure, the spectrum is labeled with a series of numbers. Each of these numbers represents the mass-to-charge (m/z) ratio or molecular weight corresponding to a particular peak. The table shown in each figure describes the relative intensity (RI) of each m/z value. The sample vials [with results shown in Figure 7(a) and (b)] contained air as the oxidizing gas. The other three vials were purged with additional oxygen in order to insure an oxygen rich environment for reaction with the active barrier materials. Figures 7(b,c) and 8(a,b), respectively, show GC-MS spectra of pure MO, PET/MO copolymer, pure CHEDM, and PET/CHEDM copolymer.

Spectra of the pure MO and the PET/MO copolymer show three major gas compounds, with m/z values of 28, 32, and 44. The gas with a molecular weight of 28 is nitrogen and that with a value of 32 is oxygen. The gas with molecular weight of 44 could be carbon dioxide or acetaldehyde. In order to verify the identification of acetaldehyde versus carbon dioxide as an oxidation byproduct of MO, pure acetaldehyde (AA), and oxidized monoolein were analyzed with headspace gas chromatography. The acetaldehyde had a peak residence time of 2.25 min as did the peak from MO oxidized for 5 days at 50°C, indicating that acetaldehyde was the major volatile oxidation byproduct.

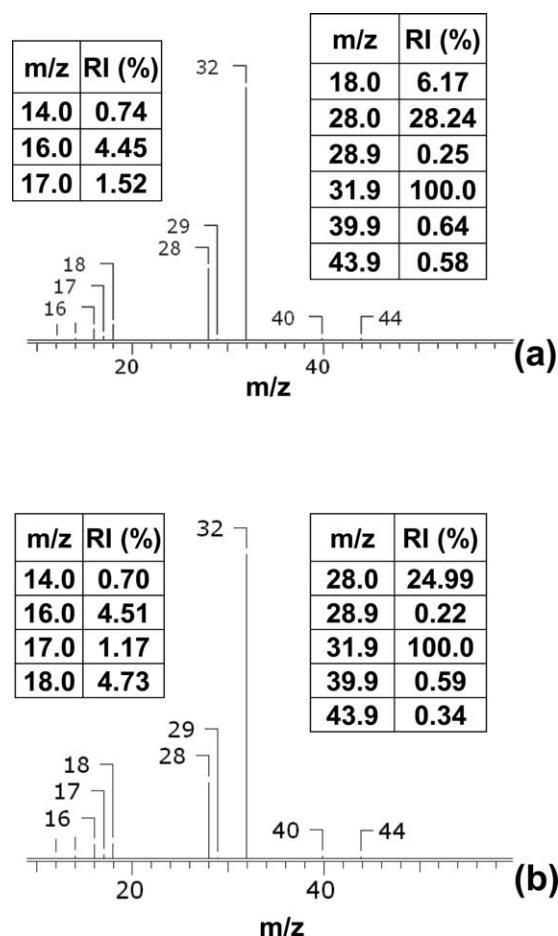


Figure 8. GC-MS spectra of (a) pure CHEDM and (b) PET/CHEDM copolymer.

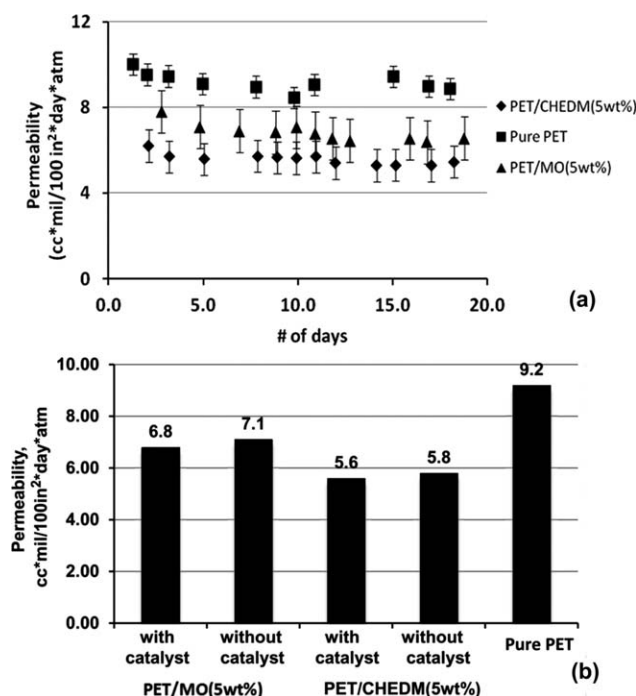


Figure 9. (a) Oxygen permeability plotted as a function of time for pure PET and for PET/MO and PET/CHEDM copolymers prepared with catalyst. (b) Average oxygen permeability for pure PET and for PET/MO and PET/CHEDM copolymers prepared with and without catalyst.

The GC-MS spectra of the exposed CHEDM and the PET/CHEDM copolymer show only two major components with m/z values of 28 and 32 that are respectively nitrogen and oxygen. It can be concluded that CHEDM and the PET/CHEDM copolymer have no major volatile oxidation byproducts. Others¹⁴ have reported that the oxidation of cycloalkenes should not result in low molecular weight products, because oxidation causes rearrangement and bond migration. Since the cycloalkene compounds do not fragment during oxidation, no volatile oxidation byproducts should be detected.

Oxygen Permeability

Oxygen barrier properties of extruded copolymer sheets samples were evaluated using a whole package MoCon tester. Cobalt octoate catalyst had been added to enhance oxygen uptake and/or improve the rate of reaction between the oxygen scavenger and permeating oxygen. It did not significantly affect oxygen barrier properties, however, since similar results were recorded for sheet samples with and without catalyst. Figure 9(a) shows plots of permeability versus number of days of exposure for pure PET and for PET/MO (5 wt %) and PET/CHEDM (5 wt %) copolymer sheets that both contained cobalt octoate catalyst. Figure 9(b) shows the average permeability values obtained for pure PET, PET/MO (5 wt %), and PET/CHEDM (5 wt %) copolymer sheets, both with and without catalyst. It can be seen that the average permeability value for the PET is 9.2 cc mil 100 in⁻² day⁻¹ atm⁻¹. Those for the MO samples are 6.8 and 7.1 cc mil 100 in⁻² day⁻¹ atm⁻¹ and for the CHEDM samples 5.6 and 5.8 cc mil 100 in⁻² day⁻¹ atm⁻¹, with slightly lower values recorded in the presence of catalyst. In comparison to the commercial PET, there are improvements of

almost 30 and 40% in the respective PET/MO and PET/CHEDM copolymer oxygen permeability values.

Copolymers of PET/CHEDM showed greater improvement in their oxygen barrier properties than those of PET/MO. The density of a polymeric material can influence its oxygen barrier properties. Densities of the copolymers containing 5 wt % scavenger were lower than that of pure PET (1.334 g cm⁻³). The density of the PET/MO copolymer was 1.313 g cm⁻³ and that of the PET/CHEDM sample was 1.322 g cm⁻³. This difference was expected because the copolymer with the more compact CHEDM should have better packing ability than that containing the long bulky MO side chains. The higher density of the PET/CHEDM copolymer is consistent with its lower oxygen permeability results.

For the initial measurement period, it was expected that very low values of permeability (or flux) for the PET/scavenger copolymers would be observed. Values were then expected to increase to reach steady state. Permeability values for the PET/scavenger copolymer samples; however, were almost constant during measurement. This could have resulted from slow reaction rates of the scavengers with oxygen in comparison to rates of oxygen diffusion. For cases when the rate of reaction is slow in comparison to the rate of diffusion, the time lag approaches that of diffusion alone and the slope of the plot of flux or permeability versus time remains almost constant.¹⁵ This is similar to the behavior observed for the PET/scavenger copolymers.

Thiele Modulus of Scavengers and PET/Scavenger Copolymers

To further evaluate effectiveness of the oxygen scavengers, the Thiele Modulus was calculated using rate data from NMR measurements. The Thiele modulus (Φ) is given by the following equation.^{11, 16}

$$\Phi^2 = k L^2 / D \quad (12)$$

Here D is the diffusivity of oxygen in the copolymer, L the thickness of the sample, and k the rate constant of oxidation. The quantity Φ^2 is a measure of the ratio of chemical reaction rate to rate of diffusion. When the Thiele modulus is large, diffusion usually limits the overall rate of reaction and when it is small, the chemical reaction is usually rate-limiting.

To calculate the diffusivity coefficients for the active barrier scavenger copolymers, we have utilized master curves developed by Van Krevelen.¹⁷ The relationships among activation energies of diffusion (E_D), sizes of the diffusing molecules (d), and glass transition temperatures (T_g) of polymers in both glassy and rubbery states are given in Van Krevelen's Figure 18.7.¹⁷ Values for E_D were estimated from his plot of E_D/d^2 versus T_g , using the T_g of 71°C for the PET/MO (5%) copolymer and d of 3.47 Å for the diffusing oxygen molecules. The estimated E_D of 39.28 kJ mol⁻¹ (9392 cal mol⁻¹), was then used to calculate diffusivity (cm² s⁻¹) at each oxidation temperature. For glassy polymers the following relationship can be used.¹⁷

$$\log D \approx \log D_0 - E_D / 2.3RT = ((-E_D / 2.3R)(1/T - 1/\Theta_2)) - 4.0 \quad (13)$$

Here $\Theta_2 = 2500 / 2.3R = 545$ K.¹⁷ At the oxidation temperature (T) of 323 K (50°C), the diffusion coefficient (D) was calculated

Table VIII. Thiele Modulus (Φ), Diffusivity (D), and Rate Constant (k) Values for PET/MO and PET/CHEDM Copolymers

Parameter	298 K (25°C)	323 K (50°C)	333 K (60°C)	343 K (70°C)
<i>PET/MO copolymer</i>				
Estimated D (cm ² s ⁻¹)	7.6×10^{-8}	2.5×10^{-7}	4.0×10^{-7}	6.1×10^{-7}
Rate constant (k) (day ⁻¹)	0.011 ^a	0.036	0.053	0.081
Thiele Modulus (Φ)	(0.026)	0.026	0.025	0.025
<i>PET/CHEDM copolymer</i>				
Estimated D (cm ² s ⁻¹)	-	3.0×10^{-7}	-	-
Rate constant (k) (day ⁻¹)	-	0.041	-	-
Thiele modulus (Φ)	-	0.028	-	-

^aExtrapolated value

to be 2.5×10^{-7} cm² s⁻¹. With a measured reaction rate (k) of 0.036 day⁻¹ and thickness (L) of 0.2 mm, eq. (12) gave a calculated Φ equal to 0.026. Similar calculations were done to obtain the diffusivities of oxygen and Φ values for the PET/MO copolymer at additional temperatures. These results are shown in Table VIII. Extrapolated 298 K (25°C) rate and appropriate estimated diffusivity values were also used to calculate Φ as noted in the table. Diffusivity for unmodified amorphous PET (T_g of 78°C) was also estimated at 298 K (25°C) using the method of Van Krevelen to obtain 9.0×10^{-8} cm² s⁻¹. This value is in fair agreement, but somewhat higher than measured values reported by others (5 to 7×10^{-9} cm² s⁻¹).^{18,19}

The same process was used to calculate the diffusivity of oxygen in the PET/CHEDM (5 wt %) copolymer with a T_g of 78°C. An activation energy of 38.45 kJ mol⁻¹ (9151 cal mol⁻¹) was obtained and the estimated diffusivity was 3.0×10^{-7} cm² s⁻¹ at 323 K (50°C). The Thiele modulus was calculated using a k of 0.041 day⁻¹ and L of 0.22 mm to obtain $\Phi = 0.028$ as given in Table VIII. For all the PET active barrier copolymers the Thiele modulus is small. The rate of reaction is therefore the rate limiting step and the rate of diffusion is fast compared to the rate of reaction.

CONCLUSIONS

This study utilized two active barrier materials and their PET copolymers, synthesized by melt polymerization of terephthalic acid (TPA) with ethylene glycol (EG) and active oxygen scavengers: monoolein (MO) or 3-cyclohexene-1,1-dimethanol (CHEDM), at concentrations of 5 wt %, in separate compositions. Methodologies were developed for determination of potential oxygen scavenging capacity, as well as scavenger oxidation kinetics and effectiveness. Kinetic parameters of the MO and CHEDM scavengers and their copolymers were determined by following oxidative changes in the unsaturated double bonds with FTIR and ¹H NMR techniques and analyzing the data using three different mathematical methods. The orders of the oxidation reactions of the pure scavengers and their PET copolymers were determined to be 1 with k values ranging from 0.03 to 0.08 day⁻¹. Acetaldehyde was the major volatile by-product for the oxidation of pure MO and the PET/MO copolymer. Pure CHEDM and the PET/CHEDM copolymer did not

produce volatile oxidation by-products, because they did not fragment after reaction with oxygen. In comparison to pure PET, respective oxygen permeability improvements of 30 and 40% were found for the PET/MO and PET/CHEDM copolymers. The average density of the PET/MO copolymer (with its long bulky side chain) was lower than that of the more compact PET/CHEDM copolymer, consistent with permeability results. The Thiele modulus was small for both PET/scavenger copolymers, indicating that the rate of oxygen diffusion was fast compared to its rate of reaction with the scavenger.

A technique has successfully been developed and established for determination of the oxygen scavenging capacity and kinetics of potential oxygen scavengers. In terms of their oxidation kinetics, the pure active barrier monomers behave in the same manner as their PET copolymers; therefore, the oxidation kinetics of pure monomers of this type may be used for evaluation of their suitability as active barrier materials, without the need to synthesize their corresponding PET copolymers.

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