Thermooxidative Reactions of Polypropylene Wax in the Molten State

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ABSTRACT: Thermooxidation of polypropylene wax was investigated in the molten state under an air-flowing atmosphere. Calorimetric measurements were performed to investigate the effect of the inclusion of 1-dodecanol as an efficient primary alcohol and to reveal the typical outlines of thermooxidation, that is, the induction time and oxidation rate. The same parameters were obtained and compared on the basis of the Fourier transform infrared (FTIR) peaks of major oxidation products, such as ketones and hydroxyl groups. The results showed that 1-dodecanol caused a change in the shape of the calorimetric thermogram and also yielded oxidized products with more clarity in color. With the Arrhenius equation, the apparent activation energy was calculated on the basis of the induction time and oxidation rate for carbonyl and hydroxyl groups individually. The obtained apparent activation energy was in agreement with the proposed mechanism based on bimolecular hydroperoxide decomposition involving dodecanol. With FTIR spectroscopy, no changes in the chain helical conformation or double-bond concentration were observed during oxidation up to 500 min. An acid value of up to 6 mg of KOH per gram was obtained at this time. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2703–2710, 2009

Key words: activation energy; infrared spectroscopy; poly(propylene) (PP)

INTRODUCTION

As effective additives, low-molecular-weight polymeric waxes are often used to control the surface properties of polymeric products. The introduction of polar groups, such as oxygenated functionalities, into the backbone of a polyolefin may improve its compatibility with other polar polymers or even with specific fillers.[1–3] This may enhance the polymer surface energy, resulting in better surface wettability and hence improved coatability. Alternatively, the surface energy of polyolefins may be enhanced by the grafting of unsaturated molecules bearing functional groups such as maleic anhydride.[4–6] It has been reported that the polar component of the surface energy of polypropylene (PP) was greatly increased by either the incorporation of an oxidized paraffin wax or the use of a maleic anhydride grafted wax.[7,8] However, because of its immiscibility with the crystalline phase of PP, the mechanical properties were adversely affected at wax concentrations exceeding 6 wt %.[8]

Recent studies have shown that the rate and extent of PP thermooxidation can be monitored by the quantitative analysis of reaction products with Fourier transform infrared (FTIR) spectroscopy,[9–11] chemiluminescence,[12] the detection and quantification of reaction exotherms with thermal analysis methods,[13] and chemical titration.[14] Moreover, some mechanisms for the thermal degradation of PP, mainly in the solid state, have been proposed.[10,15,16] The degradation reaction is believed to be free-radical-initiated and follows a chain reaction of several steps. The decomposition mode of PP is still difficult to determine clearly.[15]

In this article, we present the first systematic study of the thermooxidation of PP wax with the aim of obtaining better miscibility with the PP matrix than oxidized polyethylene-based waxes. The thermooxidative reactions of PP wax were studied with FTIR and differential scanning calorimetry (DSC) techniques. The results of these two different techniques are compared. Although there are many studies concerning the thermooxidation of PP in the solid or melt state, to the best of our knowledge, no data have been found concerning the thermooxidation of PP in the wax form.

EXPERIMENTAL

Materials and sample preparation

PP homopolymer wax (CS-52N) was supplied by Coschem Co., Ltd. (Chunbuk, South Korea). It is a white, translucent, and odorless powder with a
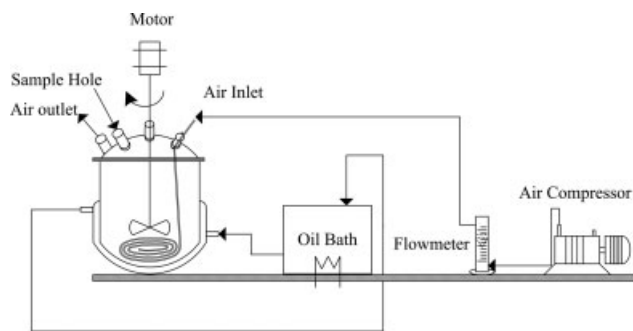
Figure 1 Schematic view of the setup used for the thermooxidation process.

softening point of 161°C and a number-average molecular weight of about 5000 g/mol. It is produced through a thermal decomposition route and has no antioxidant. Toluene from Merck was used as a solvent for PP wax. 1-Dodecanol (commonly known as lauryl alcohol) was used as received from Merck. It is a primary alcohol with a molecular weight of 187 g/mol and a boiling point of about 262°C. A peroxide agent, 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane (DHBP), was obtained from Degussa.

In the preparation of the sample, toluene was used to obtain a good dispersion of each of the aforementioned ingredients in the wax. In this way, a fine, premixed white powder was prepared after solvent removal and subsequent vacuum drying at 60°C overnight.

Thermooxidation process

The thermooxidation process was carried out through the reaction of oxygen with the PP wax chains; this created polar groups, mostly carbonyl and hydroxyl groups, on the backbone. Figure 1 shows a schematic view of the apparatus used for the thermooxidation process. The isothermal thermooxidative reactions were performed in a jacket flask in the temperature range of 170–200°C. The flask was equipped with an agitator and a flat, perforated helical air pipe to obtain a maximum dispersion of air bubbles in the molten wax. A nitrogen inlet was connected to the molten wax vessel to prevent possible wax oxidation before the air flow was introduced. 1-Dodecanol was initially fed to promote a good dispersion with molten PP wax. Then, the air flow was purged into the molten wax at a maximum rate of 3000 L h^{-1} kg^{-1} of PP wax while the melt was stirred at 500 rpm. The air flow was controlled by a gas flow meter and fixed at the maximum rate to get the highest possible conversion in the oxidation reactions. The samples for FTIR studies were taken at intervals of 10 min. The samples became yellowish and tackier during a prolonged period of oxidation.

Characterization

The isothermal thermooxidative degradation was investigated by calorimetric measurements with DSC (PL-1, Polymer Laboratories, Untied Kingdom) in a flowing air atmosphere (50 mL/min) in the temperature range of 170–200°C. In each case, 5 mg of the premixed powders of the wax and catalyst in an open aluminum pan was kept under a nitrogen atmosphere until the desired temperature was reached. The low amount of powder in the open pans ensured that sufficient gas was available around the sample. In the isothermal test, the samples were heated at a constant rate of 20°C/min from the ambient temperature to reach the set temperature of 170, 180, 190, or 200°C. Dynamic DSC tests were also carried out on open pans under a flowing air atmosphere (50 mL/min). The scans were extended up to 350°C at a constant heating rate of 10°C/min. Thermogravimetric analysis (TGA) was carried out with a PerkinElmer Pyris thermogravimetry/differential thermal analysis instrument. The curves were then recorded at a heating rate of 10°C/min from the ambient temperature to 400°C in a flowing air atmosphere.

The FTIR spectra were recorded with an Equinox 55 spectrometer (Bruker, Germany) in the wavenumber range of 400–4000 cm^{-1}. The spectra were collected at a resolution of 1 cm^{-1} to ensure the detection of small wave-number shifts in peak centers. The FTIR spectra were normalized and quantified by a carbonyl index (CI), which was calculated as the area ratio of the integral intensity of the multiple overlapping carbonyl peak (1660–1800 cm^{-1}) to that of an internal standard peak at 1167 cm^{-1} assigned to the —CH$_3$ wagging frequency.[10] The absorption bands of oxidation products such as ketones, esters, aldehydes, carboxylic acids, and lactones fell in this region, centering around 1720 cm^{-1}. In the same way, the content of hydroxyl groups was evaluated with the hydroxyl index (HI), which was calculated as the area ratio of the corresponding broad band in the range of 3250–3600 cm^{-1} to that of the internal standard peak at 1167 cm^{-1}.[9,17]

To provide a uniform film of known thickness, the molten wax was slightly pressed between two KBr pellets. On the basis of the Beer–Lambert law, at a known film thickness, the concentrations of carbonyl and hydroxyl groups could be calculated with molar absorptivity values of 300 and 70 L mol^{-1} cm^{-1}, respectively.[9]

From a technical point of view, the oxidation of PP wax can be followed by an analytical parameter such as the acid value. Because most of the oxidation products are acidic, it can be a useful technique for detecting the changes during oxidation. According to ASTM D 1386, the milligrams of KOH needed
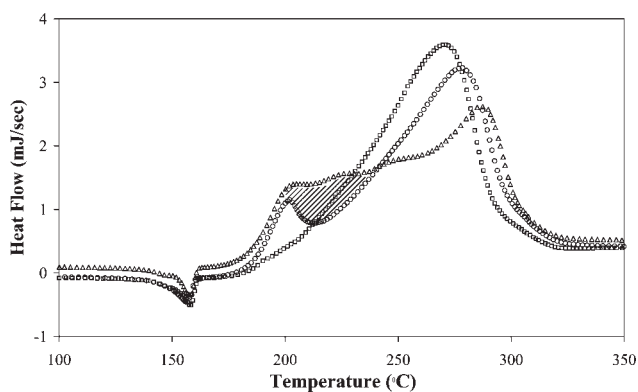
Figure 2 Dynamic DSC thermograms of PP wax under the flowing atmosphere of (□) nitrogen, (○) air, and (△) air for the specimen containing 55 mmol/kg dodecanol.

to neutralize the unit mass of dissolved wax can be measured as an acid value.

RESULTS AND DISCUSSION

Thermal analysis

The effect of 1-dodecanol on the exothermic oxidation reaction of PP wax was investigated with dynamic DSC on a premixed powder of PP wax and dodecanol. Figure 2 shows dynamic DSC thermograms of the PP wax under flowing nitrogen and air atmospheres individually and also for a specimen containing 55 mmol/kg dodecanol. The PP wax under a flowing nitrogen atmosphere shows only a peak starting at about 180°C, which is attributed to the polymer degradation. However, in the DSC thermogram of PP wax under a flowing air atmosphere, an additional peak, which is attributed to polymer oxidation, appears before the degradation exotherm. Because of the change in the flowing atmosphere to air, an exotherm of 6.3 kJ/mol evolved for the oxidation peak beginning at 188°C. The oxidation exotherm may simply originate from the appearance of oxygenated functional groups, and the degradation exotherm may originate from a macromolecular degradation process such as chain cleavage. Another feature observed in the DSC thermogram of PP wax under a flowing air atmosphere is the lower amount of the degradation exotherm and the higher maximum degradation temperature. The DSC thermogram shows a reduction in the total evolved heat (both exotherms) of about 5.77 kJ/mol and a small shift for the maximum degradation temperature. In the DSC thermogram of the specimen containing dodecanol, the presence of 55 mmol of dodecanol in a unit mass of wax (55 mmol/kg of wax) revealed an additional exothermal effect of about 12.08 kJ/mol in comparison with the thermogram of neat PP wax under a flowing air atmosphere. A part of this additional exotherm evolved between oxidation and

degradation exotherms, so a broad exotherm peak connecting both oxidation and degradation exotherms appeared in that thermogram; it is shown as the hatched area in Figure 2. It seems that dodecanol helps the oxidation reactions to continue progressively in a broader temperature range. This interaction effect can also be supported by a study already reported by Abdouss et al.[18] It has been reported to be an efficient catalyst in the thermooxidation of PP in monochlorobenzene. Such behavior in the calorimetric measurements was also observed with a premixed powder of PP wax and DHBP.

Figure 3 shows the dynamic DSC thermograms of premixed powders of PP wax and dodecanol and DHBP individually. Each species was incorporated into the PP wax at a concentration of 55 mmol/kg of wax. The dynamic DSC scan of equally premixed dodecanol and DHBP associated with PP wax is also shown in Figure 3. In this specimen, each species had a concentration of 50 mmol/kg of wax. As shown in Figure 3, for the specimen containing DHBP, a similar trend in the thermogram's shape between the oxidation and degradation peaks appeared, like that of the specimen containing dodecanol. However, the amount of the total exothermic peak was about 136.15 kJ/mol, which was about 11.9 kJ/mol lower than that of the PP wax under a flowing air atmosphere. The results for the equally premixed composition showed a more intense decrease in the exotherms, which were about 33.25 kJ/mol lower than that of the PP wax under a flowing air atmosphere. Again, it is worth noting that the amounts of heat were obtained at an air flow rate of 50 mL/min.

The mechanism for peroxide-type initiators is well recognized because they are a source of reactive oxy radicals for the initiation of a free-radical reaction on the PP backbone.[15–17] In fact, the primary peroxide radical is transferred to the PP chain mostly to form a free radical on a tertiary carbon atom.[15] The
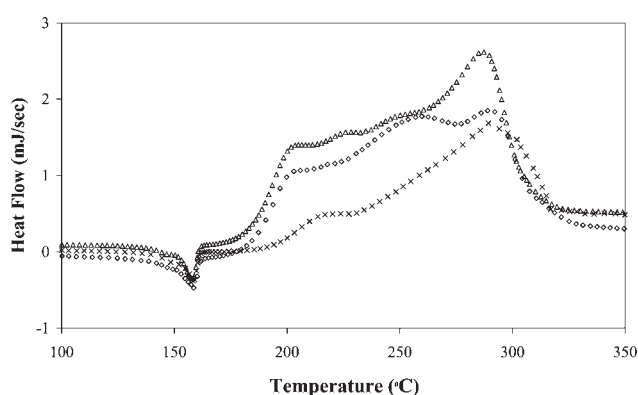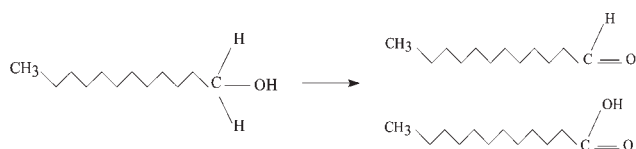

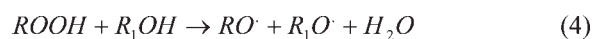**Figure 3** Dynamic DSC thermograms of PP wax in 55 mmol/kg of (∼) dodecanol and of (^) DHBP.
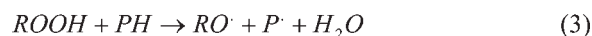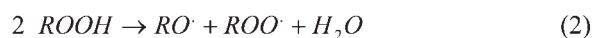
Scheme 1 Formation of acid- or aldehyde-type structures in the oxidation of alcohol.

propagation reactions result in the formation of oxygen-containing functionalities such as ketones, alcohols, carboxylic acids, esters, and lactones.[15,16] This step shows exothermal behavior in calorimetric measurements.[13] DHBP has a half-life of 95 s at 180°C. Because of its rather high decomposition half-life at the oxidation temperature, DHBP is able to provide the reaction mixture with free radicals during a prolonged period of time until its complete decomposition. It is well known that a low-molecular-weight primary alcohol has the ability to form carbonyl groups in the oxidation process.[17] During oxidation, it has been suggested that 1-dodecanol loses one or both of its α hydrogens to form acid- or aldehyde-type structures (Scheme 1).

However, the catalytic effect of dodecanol on the thermooxidation of PP wax may be preliminarily suggested in a decomposition reaction with hydroperoxide. Various possible reactions envisaged for hydroperoxide decomposition are summarized in Scheme 2.[15] It has been shown that the exothermic oxidation of PP has an autocatalytic mechanistic scheme in which hydroperoxide decomposition is a significant source of radicals.[9,11] Hydroperoxide as an important primary product decomposes into oxygen-based radicals, that is, alkoxy and peroxy radicals, and hence increases the radical concentration.

It is assumed that these radicals abstract hydrogen atoms from the polymer to yield alcohol and hydroperoxide groups as well as alkyl radicals. Reaction 1 shows unimolecular decomposition, whereas reactions 2–4 show bimolecular decomposition. The activation energy of the bimolecular decomposition of hydroperoxide is lower than that of unimolecular decomposition.[9,11] The role of dodecanol can be proposed as shown in reaction 4, in which the hydroperoxide decomposition reaction involves dodecanol. The dodecanol chain (R_1OH) is shorter than the PP chain (PH) and thus yields a shorter alkoxy chain ($R_1O^{\bullet}$). This alkoxy radical provides better mobility in the molten state and hence better reactivity. This is of great importance because the oxygen solubility decreases in the molten-state polymer.[10] In fact, dodecanol provides a more reactive alkoxy radical than polymeric alkoxy radicals ($RO^{\bullet}$) in the molten state. The alkoxy radical reacts first via an intramolecular abstracting hydrogen atom, mostly secondary

$$ROOH \rightarrow RO^{\cdot} + {}^{\cdot}OH \tag{1}$$

$$2\ ROOH \rightarrow RO^{\cdot} + ROO^{\cdot} + H_2O \tag{2}$$

$$ROOH + PH \rightarrow RO^{\cdot} + P^{\cdot} + H_2O \tag{3}$$

$$ROOH + R_1OH \rightarrow RO^{\cdot} + R_1O^{\cdot} + H_2O \tag{4}$$

Scheme 2 Proposed possible reactions for hydroperoxide decomposition.

hydrogen from the PP backbone, or via β scission into molecules with carbonyl groups and alkyl radicals.[15,16] The reaction can be intermolecular and intramolecular. In this way, hydroperoxide decomposition for radical generation induces autocatalytic thermooxidation in PP.

According to the findings of experiments with a bench-scale reactor, another difference is the clearer product with the same oxidation level with dodecanol. It may seem reasonable that dodecanol restricts undesirable side reactions, and this in turn affects the color of the product greatly. Moreover, it leads to better control of the oxidation process, giving rise to a final product free of possible hazardous residuals. On the basis of these data, dodecanol was chosen as an efficient species in all of the following experiments.

To determine the effectiveness of ingredients on PP wax thermooxidation, TGA of the premixed powders of PP wax and DHBP and of PP wax and dodecanol was examined individually with an ingredient concentration of 55 mmol/kg of wax. Figure 4 shows TGA thermograms of the premixed samples
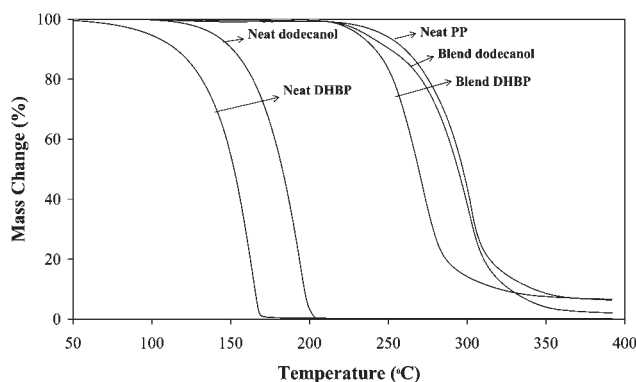

Figure 4 Thermal decomposition curves of the neat PP wax, dodecanol, DHBP, and their premixed samples. The premixed samples had the same concentration of 55 mmol/kg of wax.

in addition to those of the neat PP wax, dodecanol, and DHBP. The blends and neat PP underwent thermooxidation reactions during the test, whereas the neat ingredients underwent a thermal decomposition process. The TGA thermograms of the blends show a shift of the onset of decomposition to higher temperatures compared to those of the neat materials, that is, DHBP and dodecanol. The degradation half-temperature ($T_{0.5}$), which indicates the weight loss at a value of 50% of the initial sample weight, was found at 152 and 183°C for neat DHBP and neat dodecanol, respectively. The difference in $T_{0.5}$ for neat DHBP and dodecanol remained almost constant for their blends with PP wax. It seems that at working temperatures of 170–200°C, these species get out of the reaction media. However, the difference in $T_{0.5}$ for the blends and PP at 294°C indicates the existence of each species at higher temperatures and their subsequent reactions with the PP matrix. In other words, despite their relatively low thermal stability, they are fast and effective species in PP thermooxidation reactions. As stated in the previous section, DHBP as a radical generator is able to facilitate chain scission. The formed short chains are feasible for rapid removal by thermal treatments. The TGA thermogram of the dodecanol-containing sample shows almost the same behavior as that of neat PP wax at lower temperatures. According to the proposed mechanism in Scheme 2, dodecanol is not involved in chain scission reactions. Therefore, the lower $T_{0.5}$ value for the dodecanol-containing sample versus that of neat PP can be attributed to its good reactivity in PP thermooxidation.

A further study of the thermooxidative reaction of PP wax was performed with DSC in an isothermal mode. The experiments were carried out to detect the so-called oxidation induction time (OIT). Here, it is the time from the changeover point to air flow in an isothermal experiment to the beginning of the exothermal peak. The tangent method was used to measure the OIT. Two minutes after the set temperature was reached, the nitrogen flow was replaced by air at a rate of 50 mL/min. Another important parameter in oxidation is the oxidation maximum time (OMT), which is defined as the time interval from the changeover time to the time of the maximum point of the exothermal peak. The important oxidation parameter, the oxidation rate (OR), was chosen as the steepest slope of the oxidation exothermal peak. The results for the oxidation parameters in the temperature range of 170–200°C are reported in Table I. With an increase in the reaction temperature, a small decrease in OIT and OMT was observed, and a rather noticeable increase in OR was also observed. The results for OR are confirmed by the results for OIT and OMT. However, because of the short reaction times at elevated temperatures, it was difficult

TABLE I
Oxidation Parameters of the PP Wax at Different Temperatures Obtained from the Isothermal DSC Experiments

Isothermal temperature (°C)	OIT (min)	OMT (min)	OR ($\times 10^3$ mcal/s^2)
170	4.56	8.11	4.73
180	4.76	7.16	5.78
190	4.39	6.41	24.56
200	4.35	5.61	36.37

to determine OIT and OMT accurately. In fact, times below 10 min are not precise in this manner.[13]

FTIR spectroscopy

From FTIR studies, a representation of the variation in the intensity of the hydroxyl and multiple overlapping carbonyl groups is shown in Figure 5(a,b), respectively. The intensity of the hydroxyl and carbonyl vibration bands increases with prolonged degradation. In Figure 5(a), in addition to the increase in the intensity of the hydroxyl absorption bands, two carbonyl overtone peaks appear at 3340 and 3405 cm^{-1}. On the basis of the reports,[15,16] hydroperoxide formation may present an absorption feature in this region (3410 and 3550 cm^{-1}). It has been reported to appear before the generation of a variety of carbonyl and hydroxyl groups. Although the free and also isolated tertiary hydroperoxide is very unstable at elevated temperatures, it is difficult to detect any corresponding peaks in this study. As stated before, the thermooxidation reactions may further propagate by hydroperoxide decomposition into alkoxy- and peroxy-type radicals.

In Figure 5(b), the carbonyl absorption band around 1720 cm^{-1} can be attributed to the development of different ketone-containing groups. Further adsorptions with degradation progressing in the region of 1775–1780 cm^{-1} can be assigned to secondary oxidation products such as peracids and γ-lactones.[16] Peracids are formed via the hydrogen abstraction of an aldehyde and easily decompose into hydroxyl- and carboxyl-type radicals. If the alkoxy radical abstracts a primary hydrogen atom, oxidation can yield γ-lactone via the formation of a carboxylic acid group and a subsequent reaction with a γ-hydroxyl group.[15,16] There is also a shift in the maximum peak from 1716 to 1719 cm^{-1} in the spectrum corresponding to 200 min versus that corresponding to 50 min at 180°C. The same trend was observed more or less for other spectra at 170, 190, and 200°C. However, the shift in the maximum peak was greater for the higher oxidation temperatures, and the bands broadened. The broadening of the
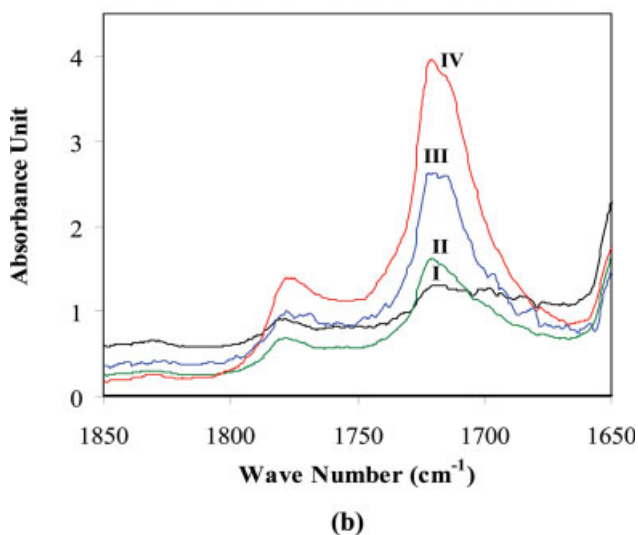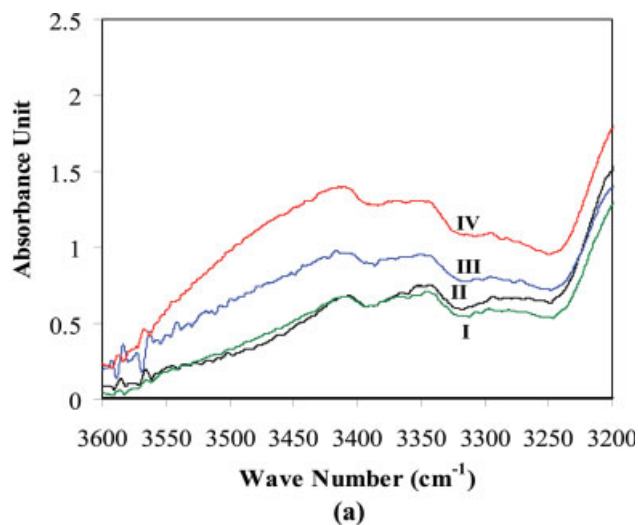
Figure 5 FTIR spectra of the specimen containing 55 mmol/kg dodecanol during oxidation at 180°C in the regions of the (a) hydroxyl group and (b) carbonyl group for different oxidation times of (I) 50, (II) 100, (III) 150, and (IV) 200 min. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

bands and the following vibrational overlay were an indication of the random formation of oxidation products. This phenomenon was confirmed at prolonged oxidation times, particularly 1000 min. Figure 6 shows the FTIR spectra of oxidized PP wax at 180°C for 100 and 1000 min. Moreover, the spectrum of an as-received sample is shown in the figure. The FTIR spectrum of the oxidation of PP waxes for 1000 min obviously shows overlapping of vibrational bands. This behavior was more intense at the wave numbers of 800–1200 cm^{-1}, so the peaks were superimposed on one another, and it seems that a relatively continuous broad peak covered all the vibrational bands in this region. It is worth noting that besides the changes in the chemical
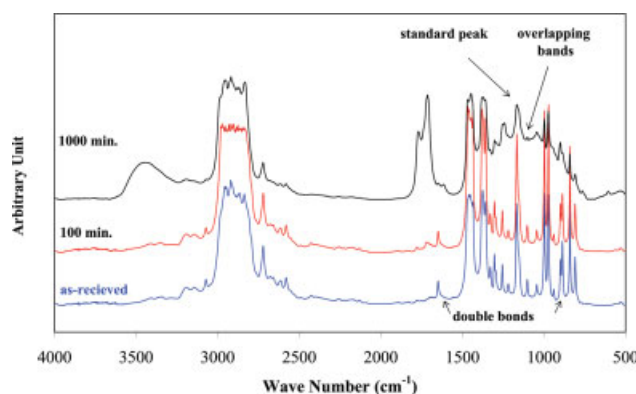

Figure 6 FTIR spectra of the as-received PP wax and oxidized PP wax at 180°C for 100 and 1000 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

compositions, changes were observed in the molecular weight distribution and chemical heterogeneity. The latter means the distribution of chemical degradation products along the macromolecule chain. It is mainly a function of crystallizability in semicrystalline polymers.[9] In this study, the wax was in a molten state and free of any crystalline regions, providing the most homogeneous state possible for the polymer to undergo the oxidation reaction. In other words, the polar groups were distributed along the wax chain, providing uniform chemical homogeneity along the macromolecule chain. This behavior in the spectrum's shape is associated with the different randomly grafted oxygenated functional groups along the chain. The change in the molecular weight distribution originates from a common cleavage mechanism in PP chains known as β scission.[10,15,16] In this way, unsaturated bonds are almost exclusively located at the end of chains. The appearance of bands at 888 and 1648 cm^{-1} in the FTIR spectrum of the as-received PP wax in Figure 6 is assigned to vinylidene unsaturation ($>C=CH_2$) and double-bond stretching, respectively.[19]

In the case of existing unsaturated bonds in aliphatic polymers, like those in the as-received PP wax, allylic hydrogen is easily abstracted. The possible mechanisms are shown in Scheme 3.[19]
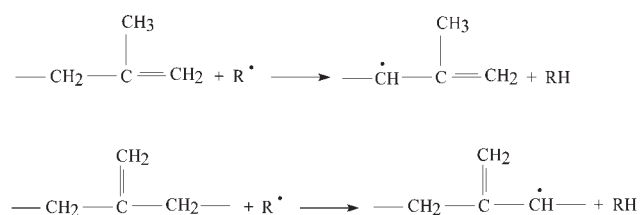
Scheme 3 Transfer reactions of radicals with polymer chains containing double bonds.

TABLE II
Acid Values and Concentrations of Carbonyl and Hydroxyl Groups After 500 min of Oxidation

Oxidation temperature (°C)	Acid value (mg of KOH/g)	Group concentration (mol/L)	
		Carbonyl	Hydroxyl
170	3.5	0.1013	0.4607
180	4.5	0.1131	0.4662
190	5.0	0.1205	0.4712
200	6.0	0.126	0.4799

Then, the allyl-type radicals will recombine with other radicals to take part in possible grafting and crosslinking reactions.[19]

In FTIR studies, the concentrations of carbonyl and hydroxyl groups can be calculated with their molar absorptivity values.[9] In Table II, the effect of the oxidation temperature on the concentration of carbonyl and hydroxyl groups and their corresponding acid values are listed for the oxidation time of 500 min. As stated before, most of the oxidation products are acidic, so the acid value is used to detect the structural changes during oxidation. As can be seen in Table II, increasing the oxidation time results in higher acid values and higher concentrations of hydroxyl and carbonyl groups. The results of the acid value confirm the carbonyl and hydroxyl group concentrations. The oxidation temperatures higher than 200°C may result in severe changes in the color of the oxidized products.

The FTIR spectra were also employed to investigate the structural changes during oxidation through the tracking of the changes in the concentration of double bonds and also the isotactic helical conformation. The intensity of the peaks at 888 and 1648 cm^{-1} was used to detect the concentration of vinylidene unsaturations and double bonds, respectively. Besides, the peak area ratio (998 cm^{-1}/973 cm^{-1}) was used as the isotacticity index.[10,19] The double-
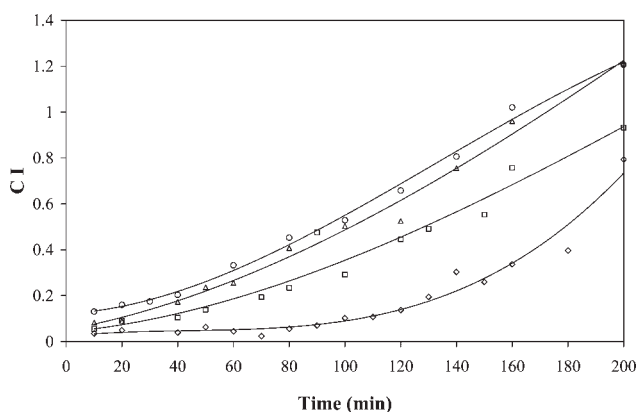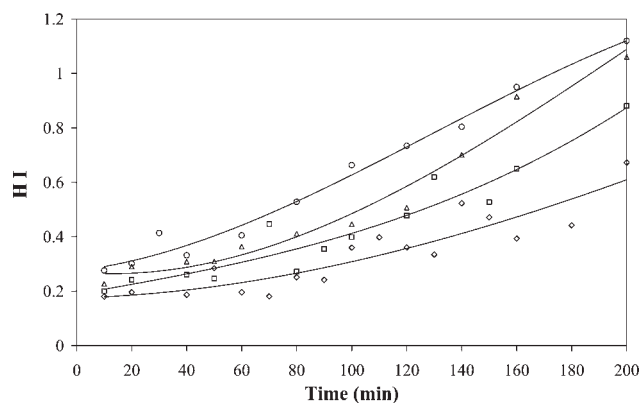

Figure 8 Variations of HI as a function of oxidation time at (◇) 170, (□) 180, (△) 190, and (○) 200°C.

bond concentration at both wave numbers remained constant during oxidation at all the studied temperatures, and the isotacticity index did not show meaningful changes. It seems that thermal oxidation leads dominantly to the formation of oxygen-containing groups on the polymer chain rather than changes in the helical conformation and double-bond concentration.

Figures 7 and 8 show the variations of CI and HI in isothermal thermooxidation reactions at 170, 180, 190, and 200°C, respectively. In both figures, the trends of CI and HI changes were fitted to a polynomial equation to determine the induction time and stationary OR. The thermooxidation reactions were carried out up to 500 min. The OMT was not observed for the whole experiment duration. As shown in Figure 7, the CI value increased as the oxidation time increased. This was more intense for higher oxidation temperatures. Similar behavior was observed for the HI value in Figure 8. However, it showed less intensity with relatively scattered data.

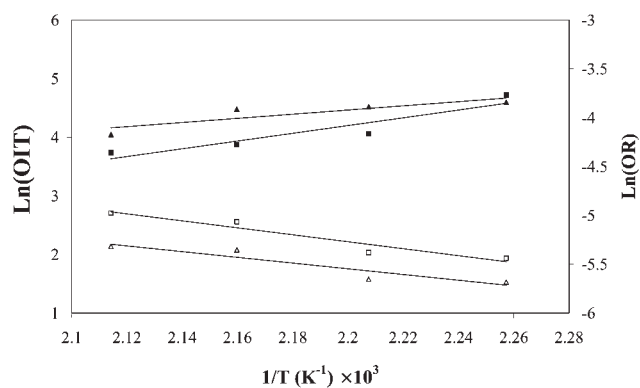The measured logarithmic values for the OIT and OR are plotted as a function of the reciprocal of the

Figure 7 Variations of CI as a function of oxidation time at (◇) 170, (□) 180, (△) 190, and (○) 200°C.

Figure 9 Arrhenius plot for Oxidation Induction Time (OIT) based on the measured (■) CI and (▲) HI and for their corresponding stationary OR values. Blank symbols are for OR (right side).

	OIT (min)		OR (10^3/min)	
	Carbonyl	Hydroxyl	Carbonyl	Hydroxyl
A	3.208×10^{-5}	3.673×10^{-2}	13.287	2.431
E (kJ/mol)	54.966	29.353	29.695	24.324
r	0.936	0.873	0.961	0.933

temperature in Figure 9. The results are based on the measured values for CI and HI. It seems that they follow the Arrhenius law. Figure 9 shows straight plots, indicating a constant activation energy for thermooxidative degradation over the studied region. On the basis of the data for carbonyl and hydroxyl groups, the pre-exponential factor, activation energy, and correlation factors are listed in Table III. In this table, the induction times are expressed in minutes, and the stationary rates are expressed in the inverse of minutes. The highest value for the apparent activation energy (55 kJ/mol) was obtained for the carbonyl induction time in PP wax thermal oxidation, the other values being relatively low. The obtained value for the activation energy seems to be lower than the data reported in the literature.[9,10,13] However, it is quite critical to compare them because of the different measuring methods that must be considered. Because the activation energy is lower for hydroperoxide bimolecular decomposition than for unimolecular decomposition,[9] this low value for the activation energy corresponds strongly to hydroperoxide bimolecular decomposition, as stated before.

CONCLUSIONS

The induction times and OR constant determined from DSC data and from FTIR data cannot result in a comparative timescale. However, the same trend was observed with increasing temperature.

Hydroperoxide is most responsible for radical generation in which autocatalytic thermooxidation is induced in PP. Although the catalytic effect of peroxide agents can be attributed to the formation of macroradicals in the initiation step of the oxidation process, the strong influence of 1-dodecanol seems to be the result of its role as a kind of unstable peroxy radical. In fact, 1-dodecanol provides more reactive alkoxy radicals than polymeric alkoxy radicals in the molten state. TGA thermograms of the dodecanol blend and DHBP blend provide evidence for fast effective ingredients in the high-temperature thermooxidation of PP.

As oxidation continues, bands of multiple overlapping carbonyl and hydroxyl groups appear simultaneously in FTIR spectroscopy. However, no changes in the helical conformation or concentration of double bonds were observed by this technique for oxidation times up to 500 min. FTIR spectroscopy is a more sensitive technique for detecting the typical outlines of thermooxidation, that is, the induction time and OR. Based on the FTIR data for carbonyl and hydroxyl groups, the measured values for the OIT and OR were used to obtain the apparent oxidation activation energy. The low value of the activation energy corresponds well to hydroperoxide bimolecular decomposition.

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