

## Gallate Derivatives as Antioxidant Additives for Polypropylene

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**ABSTRACT:** Octyl gallate (OG), dodecyl gallate (DG), and hexadecyl gallate (HG) were synthesized and characterized by Fourier transform infrared (FTIR) and NMR, and their thermal stability was measured by thermogravimetric analysis (TGA). The antioxidant effect of these derivatives in polypropylene (PP) was measured by oxidation induction temperature measurement on DSC, and by measurement of carbonyl groups in the polymer on attenuated total reflectance FTIR spectroscopy after they were aged at 120°C. The results indicated that the gallate derivatives could provide long-term stabilization to PP under conditions of oxidative degradation. The antioxidant performance of HG with longer alkyl chain was superior to the OG and DG, making the former a good candidate to be used as antioxidant additive in PP. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39850.

**KEYWORDS:** structure-property relations; properties and characterization; synthesis and processing; thermal properties

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### INTRODUCTION

Polypropylene (PP) is one of the most widely consumed and produced polyolefins in the plastics industry. It is known as one of the most important thermoplastic resin, which makes it widely applied in package, tubing, automobile, and household appliance. However, it is easy to suffer from uncontrolled oxidation during processing, storage and using, which causes undesirable changes, including discoloration and decline in mechanical properties.<sup>1–4</sup> The addition of antioxidants is an effective way to prevent PP from thermo-oxidative degradation.<sup>2,3,5</sup>

Phenols and aromatic amines, the so-called primary antioxidants, are included in stabilizer class that is characteristic of interference with the propagation step of autoxidation.<sup>6</sup> Polyphenols are widely distributed in plants and are known to exhibit higher antioxidative activities. It is considered that the presence of ortho-trihydroxyl group in the B ring and/or the attachment of a galloyl moiety contribute to the strong radical scavenging activity of the polyphenols by electron spin resonance study.<sup>7</sup> Recent research found that ortho-trihydroxyl groups can also affect the thermal oxidative stability of polymers. Zheng et al.<sup>8</sup> observed that 3',4',5'-trihydroxyphenyl of the ring in dihydromyricetin acted as an excellent antioxidant for stabilization the polymer. The structure-activity relationship of dihydromyricetin/EVA (Ethylene vinyl acetate copolymer) samples was also investigated by our research group.<sup>9</sup> The possible mechanism of action of antioxidants is that ortho-trihydroxyl group behaves as radical scavengers,<sup>10</sup> owing to the hydroxyl group in 4' of galloyl moiety group.<sup>11</sup>

The antioxidant effect of polyphenols on polymer matrix has stimulated increasing research interests, but the antioxidant mechanism has not been well-documented. Since it is difficult to disperse the gallate derivatives in nonpolar polymer due to the strong polar of ortho-trihydroxyl group, the influence of the length of alkyl chain of gallate derivatives on the antioxidative behavior in the polymer matrix has to be investigated.

Polymer antioxidants can be classified two parts: the former, known as radical scavengers, a hydrogen atom competing with the polymer substrate in the formation of peroxy radicals, thus inhibit oxidation. Secondary antioxidants, typically phosphorous- or sulfur-based compounds, can regenerate the primary antioxidant, and decompose peroxides that are intermediate products in the oxidation reactions.<sup>12</sup>

During the last decade, several research groups have focused their activities on eco-sustainable, low environmental impact and recyclable products. The gallic acid (GA) or 3,4,5-trihydroxybenzoic acid is a biologically active compound widely present in plants.<sup>13–16</sup> According to the literature, GA is also a strong natural antioxidant<sup>17–20</sup> used in pharmaceutical industry (in synthesis of trimethoprim), in food and feed industry for antioxidant making, in ink dyes and photography, and in paper manufacturing. However, there is no information about the antioxidative properties of GA in PP. However, because of its poor dispersion in PP, the application of GA as an antioxidant and functional supplement in low-polarity polymer has been restricted.

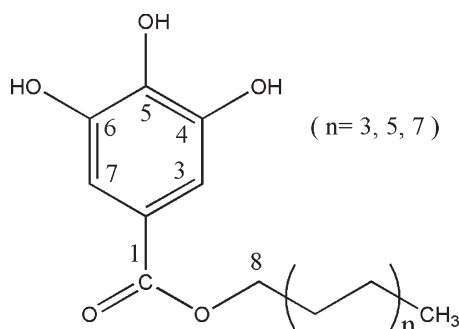


Figure 1. Structure of gallate derivatives.

With the above consideration in mind, gallate derivatives with different length of alkyl chain (Figure 1) were synthesized and employed as antioxidants for PP, and their thermal oxidation behavior for PP are investigated using long-term accelerated aging, differential scanning calorimeter (DSC), attenuated total reflection (ATR) Fourier transform infrared (FTIR) spectroscopy, and energy dispersive spectrometer (EDS).

## EXPERIMENTAL

### Materials

GA, *n*-dodecanol, *n*-octanol, 1-hexadecanol, *p*-toluene sulfonic acid, 1,4-dioxane, and other chemicals were obtained from Aladdin Chemistry Company (Shanghai, China). Isotactic PP N-T30S (MFI 3.0 g/10 min at 220°C) was supplied by Sinopec Maoming Company. All other reagents were analytical reagent grade and double-distilled water was used during the experiment.

### Synthesis of Gallate Derivatives

Esterification reactions were performed in a three-neck flask heated in an oil bath equipped with water separator, reflux, magnetic stirring bar, and a thermometer for reading the temperature for monitoring purposes. We used the same process for creating derivatives. In this work, a typical preparation of derivatives was described below [looking at the preparation of dodecyl gallate (DG), for example]: GA (7.05 g, 37.5 mmol) and *n*-dodecanol (13.95 g, 75.5 mmol) were dissolved in 50 mL 1,4-dioxane, and then *p*-toluene sulfonic acid (7.05 g, 37.1 mmol) were added to solution, the solution was refluxed at 105°C for 12 h. The progress of the reaction was monitored by TLC (Thin layer chromatography). After cooling the reaction solution, toluene was added. The precipitated material was filtered and washed with excess toluene to remove solvent and unreacted material and rinsed with excess double-distilled water then dried for 24 h in vacuum oven at 60°C.

Octyl gallate (OG), white crystal, m.p. 95–97°C. IR (KBr,  $\nu$   $\text{cm}^{-1}$ ): 3,450 (the stretching vibration of —OH), 2,952 (the stretching vibration of —CH<sub>2</sub>—), 1,668 (the vibration of C=O), 1,609, 1,467 (the stretching vibration of benzene ring skeleton), 1,258 (the vibration of —C—O—).

DG, white crystal, m.p. 96–98°C. IR (KBr,  $\nu$   $\text{cm}^{-1}$ ): 3,450 (the stretching vibration of —OH), 2,952 (the stretching vibration of —CH<sub>2</sub>—), 1,668 (the vibration of C=O), 1,609, 1,467 (the

stretching vibration of benzene ring skeleton), 1,259 (the vibration of —C—O—).

Hexadecyl gallate (HG), white crystal, m.p. 101–103°C. IR (KBr,  $\nu$   $\text{cm}^{-1}$ ): 3451 (the stretching vibration of —OH), 2,951 (the stretching vibration of —CH<sub>2</sub>—), 1,669 (the vibration of C=O), 1,610, 1,468 (the stretching vibration of benzene ring skeleton), 1,259 (the vibration of —C—O—).

### PP/Antioxidant Sample Preparation

All PP/ derivatives samples were prepared by following similar processes: PP using boiling xylene made into a slurry state and appropriate amount of each derivatives (0.4 wt %) was added with magnetic stirring. Then the PP/derivatives samples were pour into petri dish, and using high vacuum oven at room temperature for 48 h, the xylene was removed. The samples thickness of 0.5 mm was controlled by adjusting content of PP liquid and the size of petri dish. And the PP/ derivatives samples were saved for later DSC, EDS, and ATR FTIR test.

The PP/OG sample, PP/DG sample, and PP/HG samples were simplified as PP-OG, PP-DG, and PP-HG, respectively. The samples were selected to carry out thermal aging testing in an air-circulating oven at 120°C. At appropriate time intervals, the samples were taken out from the oven.

### Experimental Techniques

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained by using DRX-400 MHz NMR spectrometer. The samples were dissolved in DMSO-*d*<sub>6</sub> and TMS was used as an internal standard. ATR FTIR spectroscopy Bruker TENSOR 27 was used to test the carbonyl bands of PP films subjected to accelerated aging. The carbonyl build-up during the thermal oxidation of the samples was measured in the absorbance range between 1690 and 1800  $\text{cm}^{-1}$ , respectively. Each sample was analyzed at a fixed time and then returned to the oven for continued aging.

The thermal decomposition of samples was performed by a NETZSCH TG 209 F3 Tarsus thermogravimetric analyzer (TGA). For TGA measurement, the samples were heated from 50 to 500°C at a heating rate of 10°C/min under air atmosphere.

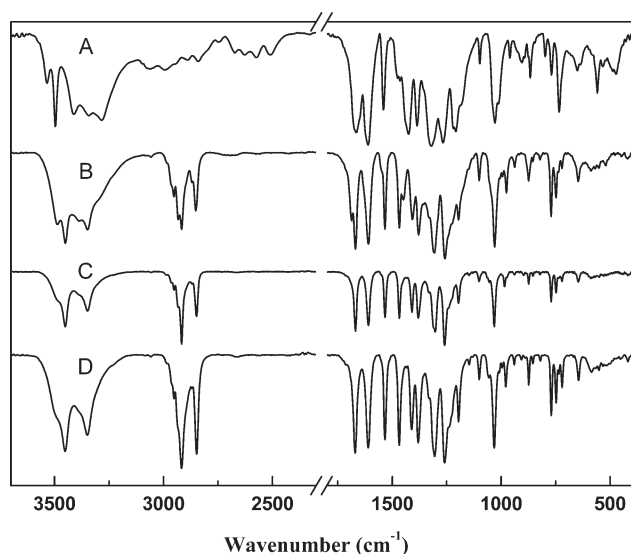
Oxidative induction temperature (OIT) of all samples was measured by a Perkin Elmer Diamond DSC as the point in the curve where the onset of the decomposition was appeared. The samples of 5–8 mg were placed in perforated aluminum pans with an air flow of 20 mL/min. Heating rate was 10°C/min. OIT was defined as the temperature when the heat flow started to change abruptly after melting peak.

EDS was used to investigate oxygen element on the sample surface. The elemental compositions of sample surfaces were operated on scanning electron microscopy Hitachi S3400N (Japan) using EDS accessory. The analysis was done in the spot modes at 15 kV. The ratios of oxygen element of the sample surface were acquired from  $W_t$  percent (weight percent) and  $A_t$  percent (atom percent) produced from the EDS automatic analysis.

## RESULTS AND DISCUSSION

### Structural Analysis of Gallate Derivatives

The derivatives were characterized by FTIR, <sup>13</sup>C NMR and <sup>1</sup>H NMR spectra. Figure 2 shows the FTIR spectra of the GA, OG,



**Figure 2.** FTIR spectra of GA (A), OG (B), DG (C), and HG (D).

DG, and HG. In the GA, the broad strong bands around 3600–2500  $\text{cm}^{-1}$  are assigned to the O—H stretching vibration of carboxylic acid and phenolic hydroxyl group. In OG, DG, and HG, the strong stretching absorption occurring at 1259  $\text{cm}^{-1}$  is the characteristic of the C—O group, likewise, the band between 3000 and 2850  $\text{cm}^{-1}$  is attributed to  $\text{CH}_3$  and  $\text{CH}_2$  groups and

asymmetric bending vibrations of alkyl chain groups appear at 1415  $\text{cm}^{-1}$ , suggesting the successful introduction of the alkyl unit into GA. In addition, the band at 3450  $\text{cm}^{-1}$  is attributed to phenolic hydroxyl, which demonstrates that the phenolic hydroxyl does not react with carboxyl group during the synthesis of gallate derivatives.

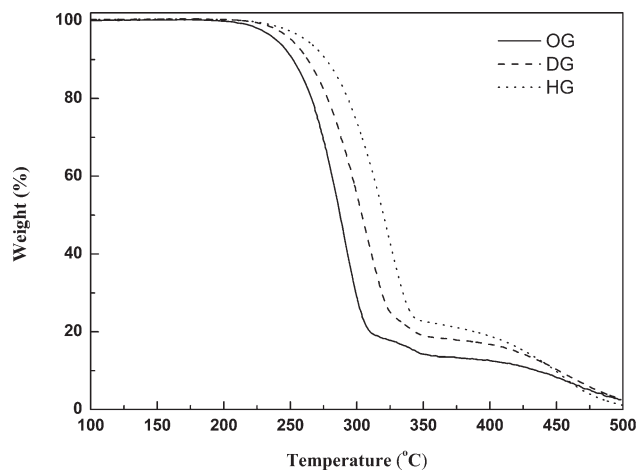
The chemical structure of gallate derivatives was further identified by  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurement, see Table I. From Table I, it can be presumed that the *n*-alkyl (methyl 0.83 ppm, methylene 1.28, 1.63, and 4.13 ppm) and the three phenol from GA (Ar—OH 8.9 ppm, two other Ar—OH 9.23 ppm, benzene ring 8.91 ppm) remain in gallate derivatives. The  $^{13}\text{C}$  NMR spectrum of gallate derivatives shows that the characteristic peak at 108.5 ppm (C (3) and C (7)), 145.5 ppm (C (4) and C (5)) and 138.3 ppm (C (5)) showed the structure has not changed. Furthermore,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum of gallate derivatives show that the characteristic peak at 4.13 ppm and 63.9 ppm, which is diagnostic for the presence of —O— $\text{CH}_2$ — in gallate derivatives. The evidence suggests that the chemical structures of gallate derivatives are determined.

#### Thermogravimetric Analysis

An additive to be effective in stabilizing polymer, it is required that the additive should be stable within the processing temperature range of the polymer.<sup>21</sup> The thermal behavior of gallate derivatives is measured by TGA at a heating rate of 10°C/min

**Table I.** The NMR Spectroscopic Data of OG, DG, and HG ( $\text{DMSO}-d_6$ )

Position	$^1\text{H}$ NMR			$^{13}\text{C}$ NMR		
	OG (ppm)	DG (ppm)	HG (ppm)	OG (ppm)	DG (ppm)	HG (ppm)
1				165.9	165.9	165.8
2				119.6	119.6	119.6
3	6.92	6.92	6.92	108.5	108.5	108.5
4	9.25	9.23	9.23	145.6	145.5	145.5
5	8.93	8.92	8.91	138.3	138.3	138.3
6	9.25	9.23	9.23	145.6	145.5	145.5
7	6.92	6.92	6.92	108.5	108.5	108.5
8	4.13	4.13	4.13	64.0	63.9	63.9
9	1.62	1.63	1.63	28.3	28.3	28.3
10	1.29	1.27	1.28	25.6	25.6	25.6
11	1.29	1.27	1.28	28.7	28.7	28.8
12	1.29	1.27	1.28	28.7	29.0	28.8
13	1.29	1.27	1.28	31.2	29.0	29.1
14	1.29	1.27	1.28	22.1	29.0	29.1
15	0.84	1.27	1.28	14.0	29.0	29.1
16		1.27	1.28		28.7	29.1
17		1.27	1.28		31.3	29.1
18		1.27	1.28		22.1	29.1
19		0.83	1.28		13.9	29.1
20			1.28			28.8
21			1.28			31.3
22			1.28			22.1
23			0.83			13.9

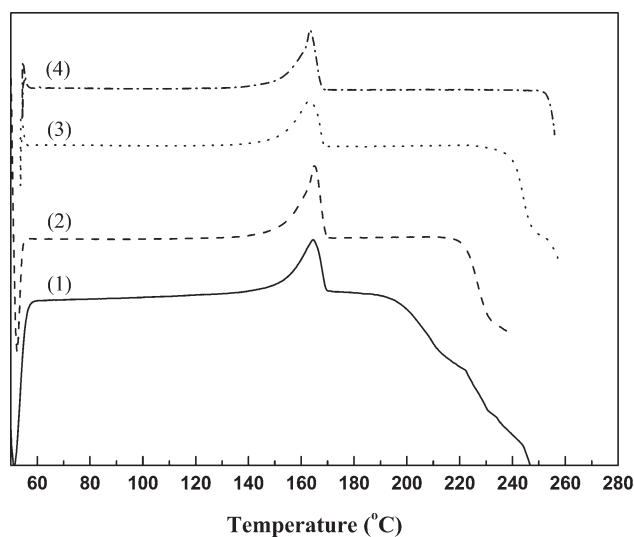


**Figure 3.** TGA curves of OG, DG, and HG at a heating rate of 10°C/min in air.

in air. Figure 3, reports the weight percent versus temperature of derivatives in air atmosphere. It is shown that all of the derivatives are relatively stable at temperature up to 220°C. It is worth noticing that the thermostability of derivatives subjected to the temperature at 5% wt loss showed an increase according to the following order: OG < DG < HG. Thus, it implies that gallate derivatives are stable at the PP processing temperature range, and they would be effective in stabilizing the polymer against thermal degradation. The result shows that an increase in the molecular of gallate derivatives enhanced their thermal stability.

#### OIT Measurements

OIT is one of the most commonly used indicators of polymer stability both in academic and industrial environment, being the preferred test used by the laboratory to assess the oxidative stability of polyolefins.<sup>22</sup> The OIT is determined by the onset of the oxidation process that is characterized by an exothermic peak in the heat flow-temperature plot.<sup>23</sup> The more resistant the sample is to oxidative degradation, the higher the OIT value. From the inset of Figure 4, it can be observed that pure PP shows a low temperature of OIT during the heating scan. The addition quantity of derivatives is 0.4 wt% for PP. The melting peaks of samples do not change with the addition of the derivatives and the melting peaks appear at about 164°C. However, the OIT of PP sample increases after the derivatives are added. As shown in Figure 4, OIT of unstabilized PP is the lowest about 196°C, while PP/derivatives samples have higher OIT than pure PP. It is because that the gallate derivatives are a kind of unhindered phenol antioxidant containing three —OH functional groups, which terminate the active free radical to generate stable free radicals to prevent the chain of PP from oxidation by supplying hydrogen atom. Gallate derivatives consisted of carbon atoms and possessed three hydroxyl groups and the average number of hydroxyl groups per molar mass of OG, DG and HG is 0.011, 0.009, and 0.007, respectively. Based on the analysis, the hydroxyl content of OG was more than all the other antioxidants. However, the thermal stability of OG shows the minimum level by means of TGA. When the thermal stability of antioxidants and the factor of molar weight were considered



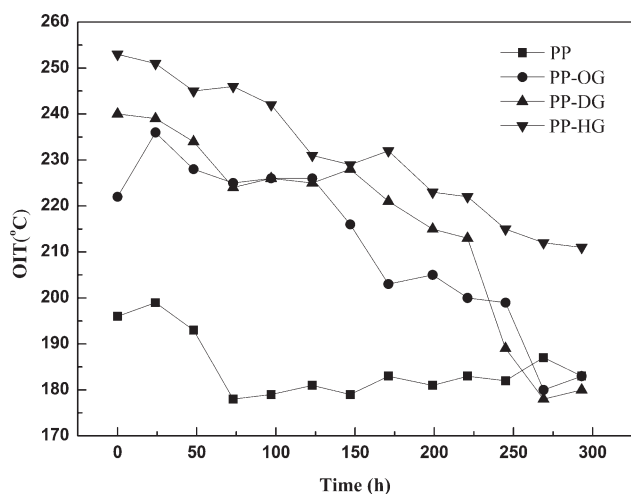
**Figure 4.** OIT curves of PP (1), PP-OG (2), PP-DG (3), PP-HG (4).

together, it is not surprising that the thermal stability of gallate derivatives has the greater impact of antioxidant in PP than the average number of hydroxyl groups per molar mass. It must be pointed out that PP-HG has higher OIT (253°C) than PP-DG and PP-OG with the OIT values of 240 and 222°C, respectively. The result implies that HG is the most effective as a thermal antioxidant of PP among gallate derivatives. The explanation is as follows: The antioxidant efficiency of gallate derivatives not only depends on its thermal stability but depends on its compatibility with PP. It is directly related to the molecular weight of gallate derivatives. Undoubtedly, HG has the longest alkyl chain, or the highest molecular weight among gallate derivatives. Therefore, the compatibility between HG and PP is better than other derivatives. For this reason, HG is the best choice as unhindered phenol antioxidant for PP.

#### Long-Term Thermo-Oxidative Stability

To measure the antioxidant effect of the gallate derivatives on the long-term stability of PP samples, the OIT values and the changes in chemical composition of the surface of PP samples with different forced aging time have been evaluated through DSC and EDS tests.

Figure 5 shows the OIT of PP-antioxidant samples at different thermal aging time in an air oven at 120°C. As shown in Figure 5, the value of the OIT decreases with an increase thermal aging time. It can be seen that the OIT value of pure PP sharply reduced to 180°C from 200°C after thermal aging at 120°C for 73 h. The PP-OG, PP-DG, and PP-HG have no below 220°C until 123, 171, and 221 h, respectively. It indicates that gallate derivatives can effectively slow down the degradation of PP. Therefore, the antioxidant efficiency of OG, DG, and HG for PP is in the order of HG > DG > OG. Generally, antioxidants has lost efficacy by two methods. One is physical loss through volatilization and migration to the surroundings. The other is chemical loss due to their antioxidant action. The antioxidant action of derivatives has similar chemical loss. However, in antioxidant efficiency the only difference of OG, DG, and HG in this system is mainly due to the former physical loss. The



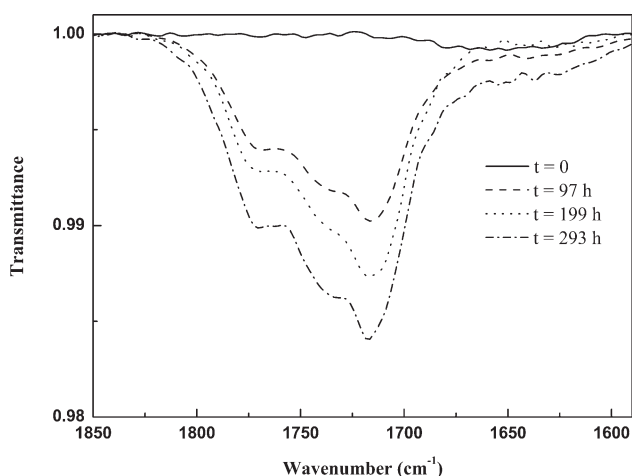
**Figure 5.** The OIT of PP, PP-OG, PP-DG, and PP-HG at increasing aging times.

antioxidant with long alkyl chain is difficult to migrate and volatilize from the PP to the surroundings, but the antioxidant with short alkyl chain has a reverse result. Therefore, the long alkyl chain plays an important role to reduce physical loss. During the long-term accelerated aging at 120°C, the values of PP-HG continues to keep the highest, therefore, the PP-HG sample is more resistant to thermal oxidation than other two derivatives.

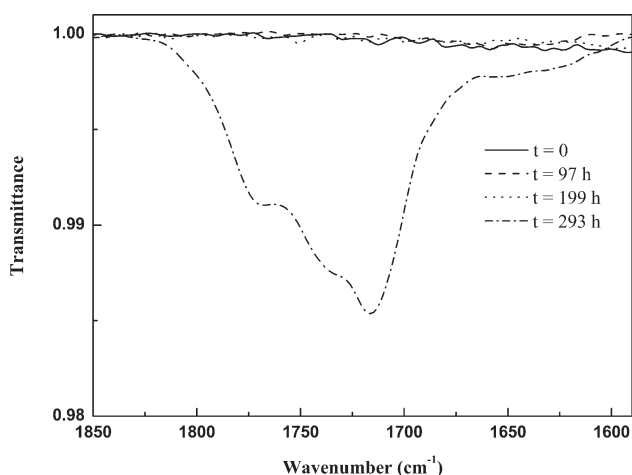
However, the antioxidant effect on the long-term stability of the gallate derivatives is performed by evaluating the number rate of oxygen atom with the EDS. It is interesting to note that there was a difference in absorption of O atom in the PP-antioxidant samples (Table II). The ratio of O in the accelerated aging samples was higher than that in PP, PP-OG, PP-DG, and PP-HG, respectively. The most credible explanation suggests that free radical reactions play a major role in the deterioration of PP samples. Many free radicals are formed due to the degradation of peroxides. As a result the oxidation products, which lead to the increases of O atom on the surface of samples, are formed. The increase rate of O atom of PP-HG (293) is found to be lower than other aging samples. Thus, the antioxidant effect of OG, DG, and HG for PP is in the order of  $HG > DG > OG$ .

**Table II.** Percentage of Oxygen Atom Versus Aging Time for PP-Based Samples

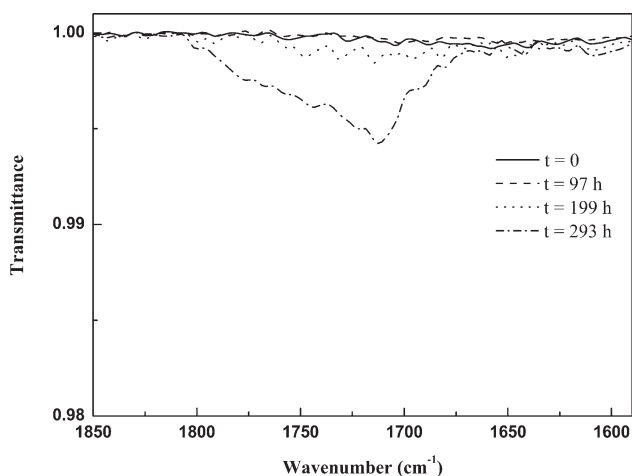
Samples [aging time (h)]	$W_t$ (%)	$A_t$ (%)
PP	1.65	1.25
PP-OG	1.55	1.17
PP-DG	1.83	1.38
PP-HG	1.58	1.19
PP (293)	6.82	5.21
PP-OG (293)	7.56	5.78
PP-DG (293)	3.04	2.30
PP-HG (293)	2.31	1.75



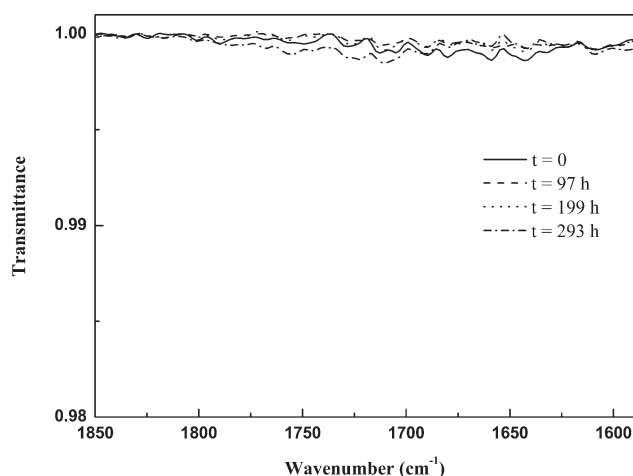
**Figure 6.** ATR-FTIR spectra in the range between 1850 and 1590  $\text{cm}^{-1}$  of PP at increasing aging times.



**Figure 7.** ATR-FTIR spectra in the range between 1850 and 1590  $\text{cm}^{-1}$  of PP-OG at increasing aging times.



**Figure 8.** ATR-FTIR spectra in the range between 1850 and 1590  $\text{cm}^{-1}$  of PP-DG at increasing aging times.



**Figure 9.** ATR-FTIR spectra in the range between 1850 and 1590  $\text{cm}^{-1}$  of PP-HG at increasing aging times.

Infrared spectrometry is a powerful tool for studying the degradation of PP and several other polymeric materials in the solid states. In the AIT-FTIR, the analytical detection of oxidation products producing from thermal oxidation degradation of PP was performed by monitoring the intensity of C=O absorption.

Figure 6 shows the ATR-FTIR spectra of PP samples in the carbonyl range at different aging times at 120°C. ATR-FTIR spectra of the PP samples show an increase of absorption in the range 1850–1590  $\text{cm}^{-1}$  over time. These changes are the result of the accumulation of carbonyl groups in the PP samples.

The main absorption bands of carbonyl groups appear at 1780, 1755, and 1725  $\text{cm}^{-1}$ . The peak at 1725  $\text{cm}^{-1}$  corresponds to the formation of ketones.<sup>24,25</sup> And the absorption at 1780  $\text{cm}^{-1}$  can be attributed to the presence of peresters or  $\gamma$ -lactones,<sup>26</sup> while the peak at 1755  $\text{cm}^{-1}$  corresponds to isolated carboxylic acids.<sup>27</sup> In this article, a similar trend of carbonyl evolution as a function of aging is also observed in the PP-antioxidant samples. In Figures 7–9, the carbonyl of absorption under the different aging time is reported for each sample, and the ATR-FTIR spectra of PP-OG, PP-DG, and PP-HG are used.

As can be observed, in the case of pure PP, the absorption bands increase with the aging time. However, the band of PP-DG does not obviously increase until aging time up to 293 h. An even more evident effect of the thermal oxidation is exhibited by PP-OG, for which the build-up is more significant. However, the carbonyl content remained low in case of PP-HG. For PP-HG the absorption band remain low even the aging time up to 293 h. Therefore, the ATR-FTIR spectra indicates that the antioxidant efficiency of gallate derivatives for PP was in the order of HG > DG > OG.

## CONCLUSIONS

A series of gallate derivatives with different length of alkyl chain were synthesized and the antioxidant efficiency of PP-based samples containing derivatives as antioxidants was studied. It is found that HG was the most effective in providing long-term stability to the PP, shown by the higher OIT over time of PP

samples. However, DSC results manifest that PP-HG has the highest OIT value (253°C), followed by PP-DG, PP-OG, and PP with the values of 240, 220, and 196°C, respectively. Based on those data, the thermo-oxidative stability of the PP-antioxidant samples follows the order: PP-HG > PP-DG > PP-OG > PP. In addition, introduction of long alkyl chains into the GA could effectively improve the stability of molecular, the compatibility of the derivatives with PP and prevent physical loss of the antioxidant from PP.

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