Evaluation of thymolphthalein-grafted graphene oxide as an antioxidant for polypropylene

Mona Bagheripour-Asl[1], Reza Jahanmardi[1,♣], Hasan Tahermansouri[2] and Erfan Forghani[1]

[1]Department of Polymer Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran
[2]Department of Chemistry, Ayatollah Amoli Branch, Islamic Azad University, Amol, Iran

Abstract

In the present work, capability of thymolphthalein-grafted graphene oxide, which was successfully synthesized in this study, in stabilization of polypropylene against thermal oxidation were investigated and compared with that of SONGNOX 1010, a commercially used phenolic antioxidant for the polymer. The modified graphene oxide were incorporated into polypropylene via melt mixing. State of distribution of the nanoplatelets in the polymer matrix was examined using scanning electron microscopy and was shown to be homogeneous. Measurements of oxidation onset temperature and oxidative induction time revealed that thymolphthalein-grafted graphene oxide modifies thermo-oxidative stability of the polymer in the melt state remarkably. However, the efficiency of the nanoplatelets in stabilization of polypropylene against thermal oxidation in melt state was shown to be inferior to that of SONGNOX 1010. Furthermore, oven ageing experiments followed by Fourier transform infrared spectroscopy showed that the modified graphene oxide improves thermo-oxidative stability of the polymer strongly in the solid state, so that its stabilization efficiency is comparable to that of SONGNOX 1010.

Key words: graphene oxide, polypropylene, antioxidant, thermal oxidation, thymolphthalein

1. Introduction

Polypropylene (PP) is a general-purpose thermoplastic material, compatible with many processing techniques. Due to its excellent mechanical properties, excellent processability and relatively low price, it is preferred over other thermoplastics in many different commercial applications. However, due to presence of a labile 3º hydrogen atom in each repeating unit of its molecules, it is prone to degradation. Among different kinds of degradation that this commodity polymer can undergo, thermo-oxidative degradation (or thermal oxidation) during its high temperature melt processing and also its service life is the most common. Chemical structure of the polymer changes upon thermal oxidation through a free radical chain reaction leading to generation of different oxidation groups such as acids, ketones, and so forth [1,2]. However, the most unwanted result of this event is reduction of molecular weight of the polymer, which, in turn, leads to weakening of mechanical properties of the polymer, which is manifested by brittleness of the polymer products [3]. Hence, over the past decades, numerous research works have been devoted to stabilization of the polymer against thermal oxidation [1]. The stabilization against thermal oxidation is generally achieved by utilization of antioxidants, which are added to the polymer with a dose of 0.05–1.0 wt%. This special additives deactivate the radicals, which are involved in the degradative reactions (referred to as primary antioxidants), or decompose hydro-peroxides, whose formation during the degradation may eventually lead to rupture of the polymer chain molecules (referred to as secondary antioxidants) [4].

Hindered phenols are one of the widely used antioxidants to stabilize PP during both the
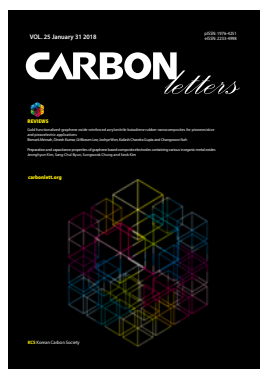
processing and the service life [5,6]. These primary antioxidants deactivate the free radicals by donating a labile phenolic hydrogen atom to the free radicals according to a general stabilization mechanism shown in Fig. 1 [7]. Thus, these antioxidants are categorized as "chain breaking donor (CBD)" antioxidants. However, the use of these strong antioxidants accompanies with some important concerns, for instance, migration of the antioxidant from bulk of polymer which dwindles the concentration of antioxidant and hence, decreases its stabilization efficiency [8]. Moreover, their molecules transform to colored compounds upon their stabilization reactions, which may change color of polymer artifacts, which, in turn, can cause some problems especially in clear polymer products [7]. Moreover, increasing performance expectations from the polymeric materials in the modern industry, such as shorter processing cycle times, which requires more intensive processing conditions require higher stabilization efficiencies. Therefore, during the recent years, many scientific efforts have been done in order to find more ef-
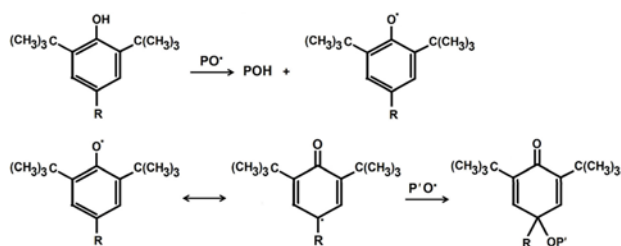
fective antioxidants, hence, efficiency of in-situ stabilization by lignin, immobilization of antioxidants within an inorganic host structure and antioxidant grafted nanoparticles in thermo-oxidative stabilization of polymer have been examined [9-11].

In 2008 Jahanmardi and Assempour [12] studied efficacy of galbanic acid in thermo-oxidative stabilization of linear low-density polyethylene. Their study demonstrated that galbanic acid improves thermo-oxidative stability of the polymer strongly in solid state and moderately in melt state. They also introduced a mechanism for the stabilizing action of galbanic acid where allylic hydrogen atoms that are present in its molecular structure play the main role.

Recently, effects of another chemical compound, which has allylic hydrogen atoms in its molecular structure, i.e., 3,3-bis(4-hydroxy-2-methyl-5-propan-2-ylphenyl)-2-benzofuran-1-one,

Fig. 1. Generally admitted mechanism for deactivation of alkoxy radicals by phenolic antioxidants [7].
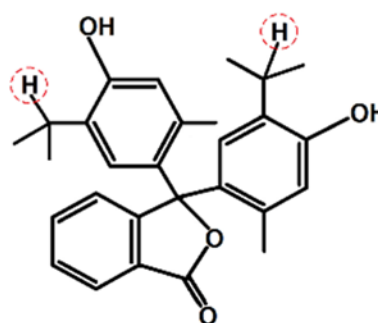

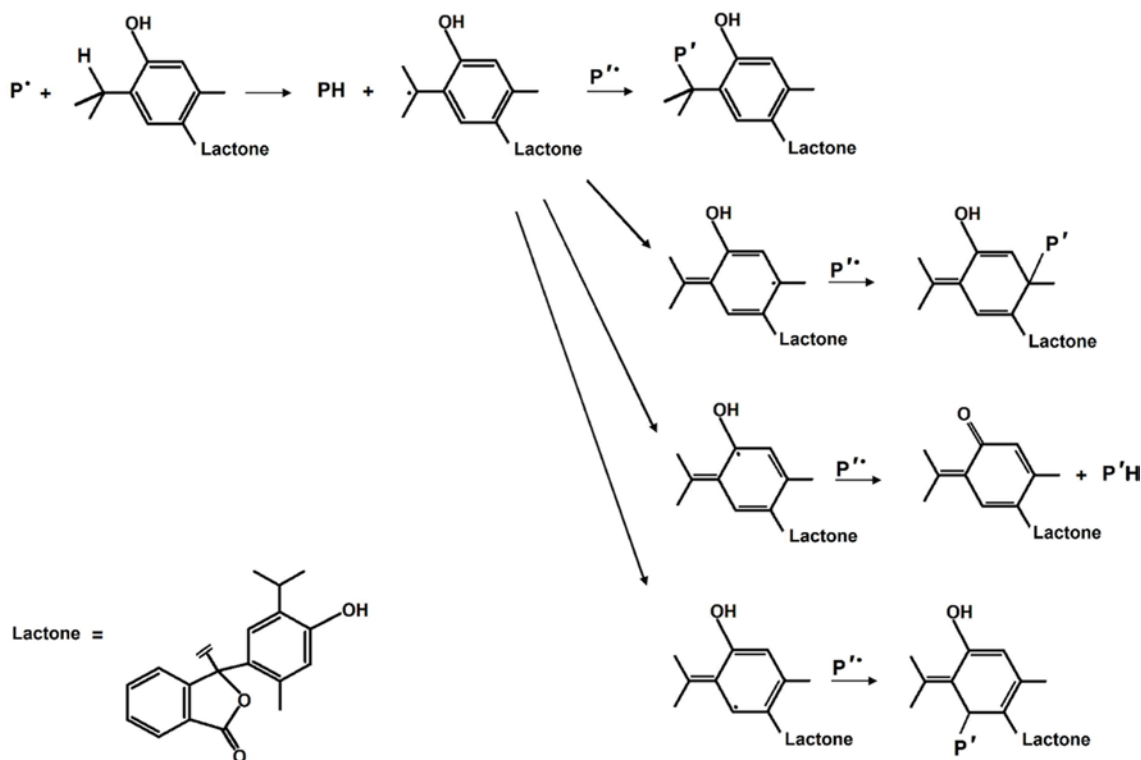Fig. 2. Molecular structure of thymolphthalein [14].

Fig. 3. Proposed mechanism for the thermo-oxidative stabilization action of thymolphthalein [15].

commonly known as thymolphthalein, on thermo-oxidative stability PP were studied [13]. It was observed that thymolphthalein, with a molecular structure shown in Fig. 2 , increases thermo-oxidative stability of the polymer outstandingly in both solid and melt states and its stabilization efficiency was shown to be comparable to that of SONGNOX 1010, an efficient commercially available phenolic antioxidant for the polymer.

Moreover, in another research work, thermo-oxidative stabilization efficiency of thymolphthalein in high density polyethylene as well as mechanism of the stabilization were investigated [15]. It was shown that two allylic 3° hydrogen atoms of thymolphthalein molecule, which are encircled in Fig. 2, are the main hydrogen atoms that take part in the reactions resulting in the stabilization of the polymer and the phenolic hydrogen atoms of thymolphthalein do not play an important role in the stabilization action of thymolphthalein. On the basis of the mentioned findings, a probable mechanism for the stabilization action of thymolphthalein was proposed, which is illustrated in Fig. 3.

However, because of small size of thymolphthalein molecules and also its low solubility in PP, which is due to dissimilar polarities of the polymer and the additive, it is expected that the additive has a high tendency to migrate from the bulk of the polymer. This can undesirably affect long-term stabilization efficiency of the additive. So, in the present work we tried to modify the new antioxidant, so that, it has no tendency to migrate from the bulk of polymer. Our strategy to achieve the goal was grafting of thymolphthalein onto graphene oxide nanoplatelets. Besides, effects of the prepared graphene oxide-grafted thymolphthalein on thermo-oxidative stability of PP matrix in both solid and melt sates were investigated.

2. Experimental

2.1. Materials

PP (HP510M grade) with MFI of 9.0 g/10 min, density of 0.90 g/cm^3 and crystalline melting point of 167°C was provided by Jam Petrochemical Co. (Iran); SONGNOX 1010 as a commercially used phenolic antioxidant, with melting point of 118°C was purchased from Songwon Industrial Co. (South Korea); Graphene oxide nanoplatelets with the specifications shown in Table 1 were purchased from Nanosany Corporation (Iran) and were used as received; Thymolphthalein and all the chemicals used for the grafting reaction, i.e., thionyl chloride, dimethylformamide (DMF), acetone, pyridine and toluene were obtained from Merck Co. (Germany).

Table 1. Specifications of the used graphene oxide nanoplatelets

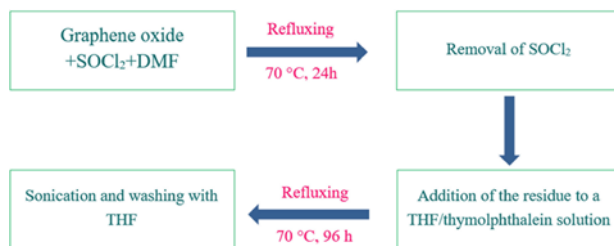| Properties	Fact
Purity (%)	99
Thickness of platelets (nm)	3.4–7.0
Diameter (µm)	10–50
Specific surface area (m^2 g^{-1})	100–300
Carbon and oxygen content (%)	C=92.7, O≤7.3

Fig. 4 . A schematic representation for the adopted functionalization process of graphene oxide.

Table 2. Sample designations

Sample designation	Polypropylene (wt%)	SONGNOX 1010 (wt%)	Modified graphene oxide (wt%)
PP	100	-	-
S1	99.9	0.1%	-
G2	99.8	-	0.2%
G5	99.5	-	0.5%

2.2. Sample preparation

Thymolphthalein was grafted onto graphene oxide nanoplatelets through a two-step esterification reaction with the aid of thionyl chloride as follows: 100 mg of graphene oxide were first suspended in a mixture of 15 mL thionyl chloride (SOCl$_2$) and 0.5 mL of DMF. The mixture was then stirred at 70°C for 24 h under reflux. Then, the residual SOCl$_2$ was removed by reduced pressure distillation to yield the acyl chloride-functionalized graphene oxide, which was subsequently added to a solution of 10 mL THF and 250 mg of thymolphthalein and the reaction mixture was stirred at 70°C for 96 h. Then, the mixture was cooled down to room temperature, filtered and washed thoroughly with THF. Subsequently, the grey solid powder was dried at room temperature for 6 h under vacuum condition. The overall procedure of this reaction is schematically shown in Fig. 4.

Melt mixing using a Brabender internal mixer was carried out in order to prepare the samples. Accordingly, PP was mixed with certain amounts of the additives at 190°C in during 6 min at rotor speed of 60 rpm. Designations of the samples together with their formulations are listed in Table 2. The prepared samples were subsequently converted into thin films with thickness of about 200 (±20) µm using compression molding at 190°C and 100 bar within 4 min.

2.3. Characterization

The occurrence of grafting reaction was examined by Fourier transform infrared (FTIR) spectroscopy using a Thermo Nicolet FTIR spectrophotometer (USA). Also, thermogravimetric analysis (TGA) using a Netzsch 209 F1 model thermal analyzer (Germany) as well as scanning electron microscopy (SEM) using a Tescan-Mira3 instrument (Czech) were used in order to

investigate the functionalization of graphene oxide. For TGA experiments, samples of about 10 mg weight were heated from 20°C to 600°C at a constant heating rate of 20°C/min under a stream of nitrogen with a flow rate of 50 mL/min. State of distribution of the nanoplatelets in the prepared composite samples was also examined by SEM using the above mentioned instrument. The samples were coated with a thin layer of gold before the SEM experiments.

2.4. Thermo-oxidative degradation of the samples in melt state

Oxidative stability of the samples in melt state was examined using two different standard tests, namely, oxidation onset temperature (OOT) and oxidative induction time (OIT). The both tests were separately carried out using a DuPont 910 DSC thermal analysis system (USA).

In the OOT test, the temperature of each sample (of about 10 mg weight) was elevated at a constant rate of 10°C/min from 25°C to 300°C. Samples were kept in aluminum pans and subjected to an oxygen environment with a flow rate of 50 cm³/min. The amount of OOT for each sample was derived from its DSC curve as the temperature corresponding to the deviation from the baseline after melting (beginning of the exothermal oxidation).

OIT test was performed according to ASTM D 3895. Hence, each sample of about 10 mg weight was heated from 25°C to 200°C at 20°C/min under a nitrogen flow while being kept in aluminum pans. After that the temperature was reached to 200°C and equilibrated, the inputting gas stream was immediately switched from nitrogen to oxygen. Flow rates of the both gases were adjusted at 50 cm³/min. The OIT value of each sample was specified from its DSC thermograms as the time interval from oxygen introduction until the commencement of exothermal oxidation reaction.

2.5. Thermo-oxidative degradation of the samples in solid state

A common accelerated ageing test was carried out to evaluate thermo-oxidative stability of the PP film samples in solid state. Thus, 4×8 cm strips of the samples were placed in a forced convection oven at 90°C. The tested samples were taken out from the oven at different aging times and subjected to FTIR spectroscopy in order to monitor their chemical changes upon to oven ageing. FTIR spectra at were taken using the aforementioned instrument as average of 20 scans at a resolution of 4 cm⁻¹ in the range of 4000–400 cm⁻¹. Kinetics of thermo-oxidative degradation of the prepared film samples were studied via determination of carbonyl index (CI) at different aging time intervals, according to the Eq. 1.

$$CI = \frac{A_{1709}}{A_{899}} - CI_0 \tag{1}$$

where, A is the absorbance at the given wavenumber and CI_0 is the original carbonyl index. In order to minimize the errors originating from the samples thickness absorption band at 899 cm⁻¹ was chosen as an internal thickness band. CI_0 were subtracted in order to exclude the effect of the original carbonyl groups. Hence, the calculated carbonyl indices only reflect the changes took place due to the thermal oxidation in the solid state.

3. Results and Discussion

3.1. Characterization of the chemically modified graphene oxide

Thymolphthalein has two phenolic groups that can react with carboxylic acid groups located at the edges of graphene oxide platelets. FTIR spectra of thymolphthalein, graphene oxide and the chemically modified graphene oxide are presented in Fig. 5. In the FTIR spectrum of thymolphthalein (Fig. 5a) absorption bands due to stretching vibration of OH group at the 3374 cm⁻¹, stretching of C-H bond in methyl and methenyl groups at 2962–2868 cm⁻¹, stretching of esteric carbonyl group at 1736 cm⁻¹, stretching of esteric C-O group at 1100 cm⁻¹ can be seen [16]. In the FTIR spectrum of graphene oxide (Fig. 5b) its characteristic absorption bands, i.e. stretching vibration of OH group at the 3394 cm⁻¹, stretching of carbonyl group at 1715 cm⁻¹, skeletal vibration of the unoxidized graphitic domains or physically absorbed moisture at 1623 cm⁻¹, OH bending at 1407 cm⁻¹, C-O stretching of epoxide at 1218 cm⁻¹, C-O stretching of alcoholic group at 1178 cm⁻¹, stretching of carboxylic C-O group at 1047 cm⁻¹ are present [17,18]. It is seen that the characteristic broad absorption band of carboxylic OH group in the 3500–2000 cm⁻¹ range of the FTIR spectrum of graphene oxide has changed to a narrower band in that of the modified graphene oxide at 3428 cm⁻¹. The latter absorption band is ascribed to stretching vibration of hydroxyl groups, including unreacted carboxylic OH groups, intact alcoholic groups on the surface of graphene
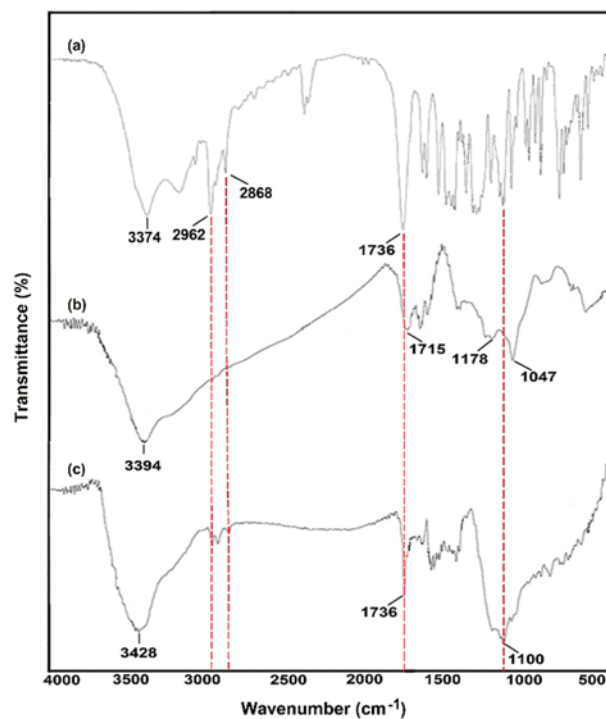

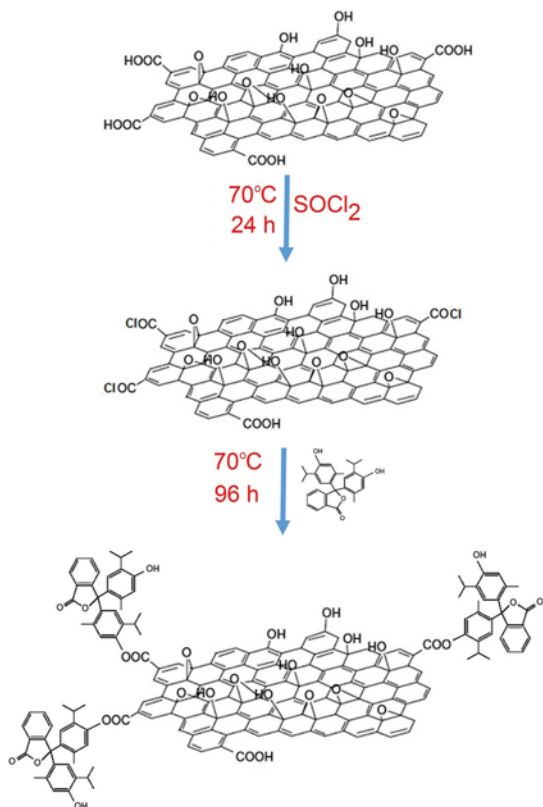**Fig. 5.** FTIR spectra of (a) graphene oxide and (b) the chemically modified graphene oxide.

Fig. 6. Schematic representation of the chemical reactions involved in the functionalization of graphene oxide with thymolphthalein.

oxide and probably hydroxyl groups of the grafted thymol-phthalein. Moreover the emergence of two new absorption bands in the FTIR spectrum of the modified graphene oxide at 1736 and 1100 cm^{-1} corresponding to stretching vibration of esteric carbonyl and C-O groups, respectively, proves that thymolphthalein was successfully grafted onto graphene oxide according to the reactions illustrated in Fig. 6. However, as this reaction is not believed to have a 100% yield, it is expected that a small portion of the carboxylic acid moieties on the graphene oxide layers remain in the final product.

Also, TGA was used to further investigate the occurrence of the grafting reaction. Fig. 7 illustrates TGA graphs of thymolphthalein, graphene oxide and the modified graphene oxide, respectively. As it is seen in the figure, upon heating up to 600°C, thymolphthalein experiences an overall weight loss of about 93%. Besides, TGA curve of graphene oxide represents two stages of thermal degradation. At the first stage, graphene oxide shows 13% weight loss up to 120°C most probably due to moisture evaporation. At the second stage, through heating up to 220°C, it further loses 48% of its initial weight which is believed to be due to elimination of labile oxygen-containing functional groups [18,19]. On the other hand, the TGA curve of the modified graphene oxide illustrates four stages of thermal degradation pertaining to the mass losses of 0.5, 3.5, 19% and 6%, respectively, which leads to a total weight loss of 29% up to 600°C. It is seen that the amount of the residue formed at the end of TGA experiment of the modified graphene oxide is significantly higher compared to that of the graphene oxide. This indicates that thermal stability of the
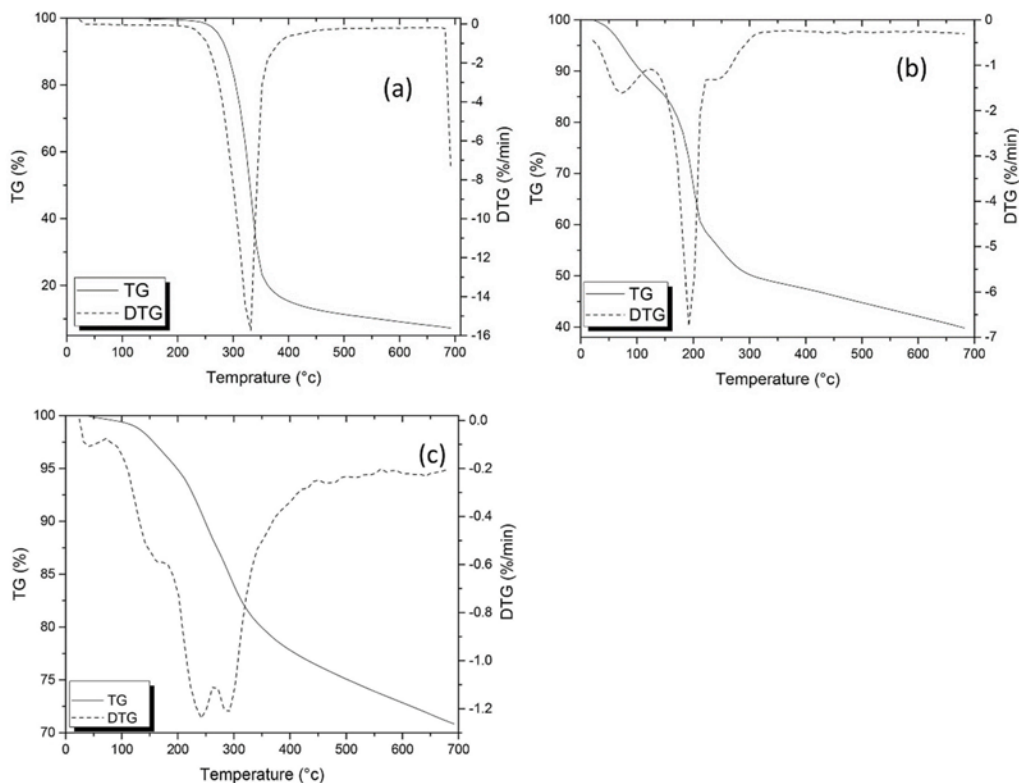

Fig. 7. TGA and DTG curves of (a) thymolphthalein, (b) graphene oxide (c) thymolphthalein-grafted graphene oxide.
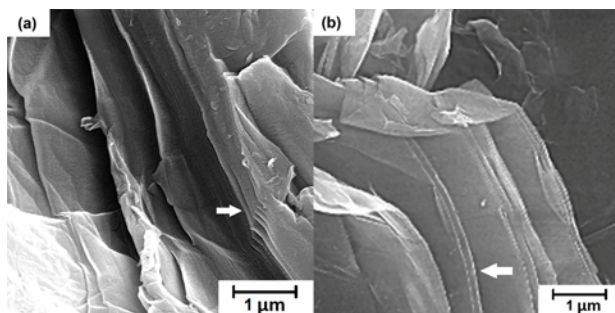
Fig. 8. SEM images of (a) graphene oxide and (b) thymolphthalein grafted graphene oxide with magnification of 30 kx.
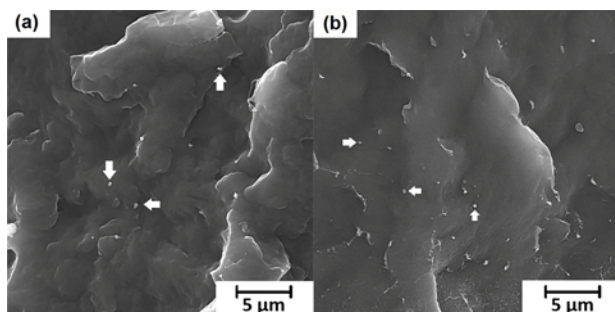

Fig. 9. SEM images of the PP sample containing (a) 0.2 wt% and (b) 0.5 wt% of thymolphthalein-grafted graphene oxide with magnification of 5 kx.

3.2. Evaluation of antioxidant efficiency of the chemically modified graphene oxide

Stability of PP against oxidative degradation in melt state can be evaluated with the aid of several analytical techniques, among them determination of values of OOT and OIT are two of the most commonly used ways. Thus, in order to quantify the effect of the modified graphene oxide in stabilizing the PP against thermo-oxidative degradation in melt state, the both OOT and OIT values were measured separately for all the samples. The measured values of OOT and OIT for the samples are presented in Figs. 10 and 11, respectively. As it can be seen in the figures, both OOT and OIT values of the both G2 and G5 samples are higher than those of the PP sample. Hence, it can be inferred that thymolphthalein-grafted graphene oxide plays an antioxidant role in the polymer melt. Meanwhile, both OOT and OIT values of the G5 sample are higher than those of the G2 sample, implying that the observed stabilization effect of the modified graphene oxide increases with enhancement of concentration of the additive. However, the amounts of the improvement in the
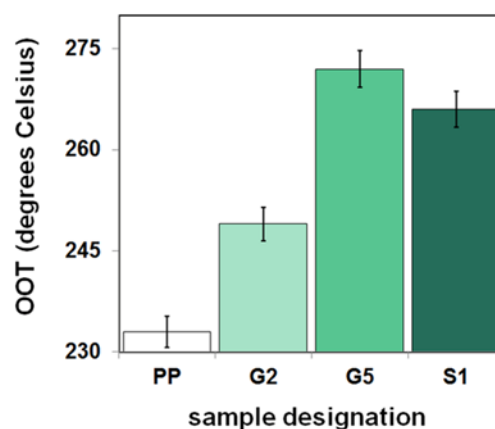

Fig. 10. The values of oxidation onset temperature (OOT) obtained for the samples.

modified graphene oxide is considerably higher than that of graphene oxide which can be attributed to the transformation of labile carboxylic acid groups of graphene oxide to more stable ester groups through the reaction with thymolphthalein. Similar results were reported by Yuan et al. [18] during their attempts for modifying graphene oxide by amine functional groups.

Moreover, according to DTG graphs, maximum degradation rate of graphene oxide and thymolphthalein occurs at about 190°C and 335°C, respectively. As a result of successful grafting reaction of thymolphthalein on graphene oxide platelets, the modified graphene oxide represents a bi-modal DTG curve, in which, the two maximum degradation rates lie at 240°C and 290°C, respectively, which are between those of thymolphthalein and graphene oxide.

Fig. 8 shows SEM images of graphene oxide and thymolphthalein-grafted graphene oxide. Some interlayer distances are pointed in the both images. According to these images, it is clear that grafting of thymolphthalein onto the graphene oxide layers increased the average interlayer distance in the graphene oxide platelets.

In addition, the SEM image taken from the fracture surface of PP samples containing 0.2 and 0.5 wt% of thymolphthalein-grafted graphene oxide, i.e., G2 and G5 samples, respectively, are shown in Fig. 9. The bright points in these images manifest the nanoplatelets implying a homogeneous distribution of the nanoplatelets in the matrix.
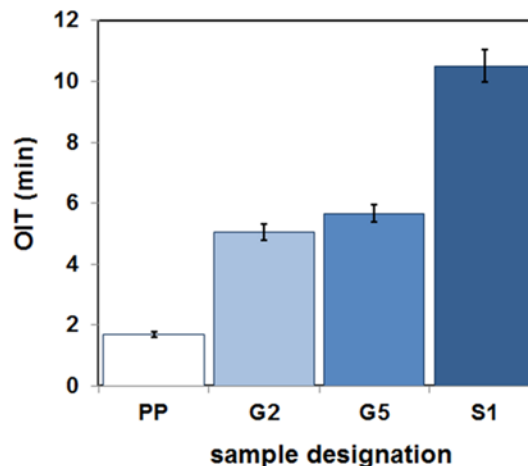

Fig. 11. Values of oxidative induction time (OIT) obtained for the samples.

both OIT and OOT values of the polymer in the presence of the modified graphene oxide are less than those obtained in the presence of SONGNOX 1010, in the case of S1 sample. As the rate of thermal oxidation in the molten state is quite high, antioxidant molecules must possess high mobility to be able to scavenge free radicals rapidly enough. Accordingly, the observed phenomenon can be attributed to the higher mobility of the SONGNOX 1010 molecules in the molten polymer matrix comparing to that of the much bulkier nanoplatelets.

The oxidation of PP results in formation of several oxygen-containing groups on its chain molecules among them carbonyl groups are the most important. The presence of carbonyl groups can be readily ascertained from their FTIR absorption band at wavenumber range of 1800–1700 cm^{-1}. Accordingly, the thermo-oxidative degradation of the PP film samples were assessed by monitoring the changes in their FTIR spectra occurred during the ageing at 90°C. The FTIR spectra of the PP and G2 samples before and after ageing for 670 h at 90°C are demonstrated in Figs. 12 and 13, respectively. In these figures, characteristic absorption bands of PP, i.e. stretching vibrations of C–H bonds, belonging to methyl, methylene and methenyl groups, at 2951–2839 cm^{-1}, bending vibrations of the C–H bonds at 1458 cm^{-1} and 1375 cm^{-1}, bending deformation of isopropyl group at 1167 cm^{-1}, out of plane bending of C–H bonds in different substituted terminal vinyl groups at 997, 972, 899, 840 and 808 cm^{-1} can be seen [16].

Besides, by taking the evolution of carbonyl absorption band in Fig. 12 into consideration it can be seen that the carbonyl absorption band in the spectra of PP sample exhibits a drastic growth in intensity upon oven ageing for 670 h. In contrast, the spectra in Fig. 13 show a slight evolution of carbonyl groups during the same time of ageing. Hence, the role thymolphthalein-grafted graphene oxide as an effective antioxidant for the polymer at a concentration of 0.2 wt% during oven ageing at the aforementioned conditions can be concluded.

Also, Fig. 14 illustrates the variations of carbonyl index of the film samples during oven ageing at 90°C. As it is seen in the figure, the incorporation of the modified graphene oxide into PP had a significant effect on the stability of the polymer, so that the induction time of the thermal degradation of the polymer was extended from almost 0 h in the case of the neat PP sample to 500 h and 670 h for the G2 and G5 samples, respectively. In addition, the induction time for the G5 sample is significantly more than that of I1 sample implying the outstanding capability of the modified graphene oxide in stabilization of the polymer against thermal oxidation in solid state. However, both G2 and G5 samples show relatively higher rate of increase in CI after their respective induction times compared to that of the PP and I1 samples. One reason behind this phenomenon can be the existence of residual carboxylic acid groups on the edges of graphene oxide layers, which accelerates thermo-oxidative degradation of the polymer after the induction time. Similar results were reported by Broska et al. [20] in thermal oxidation of PP in the presence of stearic acid and the phenomenon was attributed to a bimolecular interaction between carboxylic acid and hydroperoxide, which results in the faster oxidation of PP. Another reason can be adsorption of initially existed antioxidant molecules on the surface of the modified graphene oxide [21].
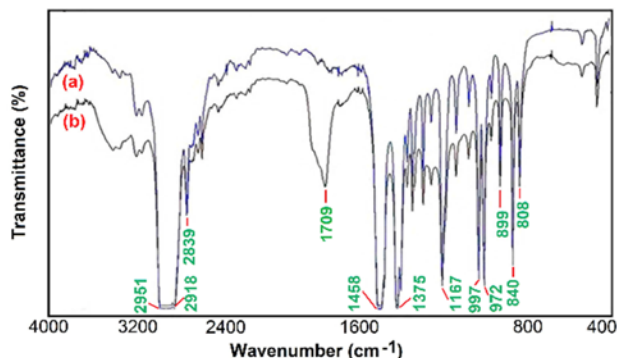

Fig. 12. FTIR spectra of the Blank sample (a) before and (b) after oven aging at 90°C for 670 h.
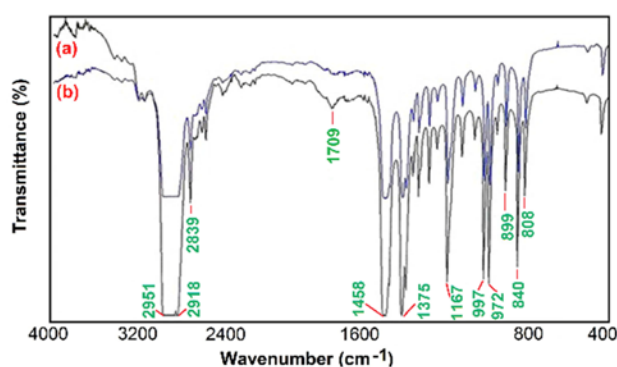

Fig. 13. FTIR spectra of the G2 sample (a) before and (b) after oven aging at 90°C for 670 h.
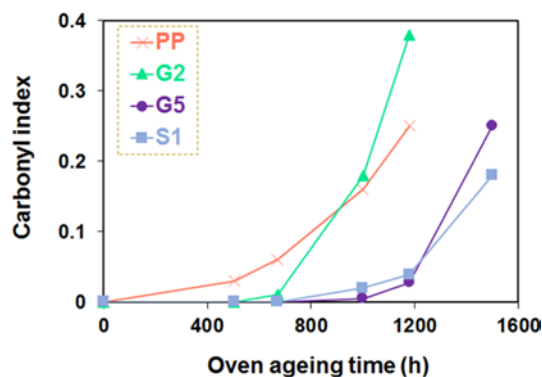

Fig. 14. Variations of carbonyl index of the film samples during oven aging at 90°C.

Accordingly, amount of the antioxidant molecules, which retard auto-oxidation reactions after the induction time, may be lower in G2 and G5 samples with respect to the PP sample.

4. Conclusions

Thymolphthalein was successfully grafted on graphene oxides nanoplatelets as a result of the reactions between its phenolic groups and carboxylic acid groups located at the edges of

graphene oxide layers. FTIR spectra and TGA graphs affirmed the grafting of thymolphthalein into graphene oxides platelets. According to SEM images presence of thymolphthalein on graphene oxide leads to increase of distance between graphene oxide layers. It was shown that the synthesized thymolphthalein-grafted graphene oxide operates an antioxidant role in molten PP and its stabilizing effect is increased by increasing its concentration. According to FTIR spectra of the film samples, which were taken during oven aging at 90°C, introducing of the modified graphene oxide in the polymer prolonged induction time of the thermal oxidation indicating the ability of thymolphthalein-grafted graphene oxide as an effective antioxidant in the thermo-oxidative stabilization of the polymer in the solid state.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

References

[1] Bertin D, Leblanc M, Marque SRA, Siri D. Polypropylene degradation: Theoretical and experimental investigations. Polym Degrad Stab, **95**, 782 (2010). https://doi.org/10.1016/j.polymdegradstab.2010.02.006.

[2] Meng X, Jiang Z, Xin Z, Chen W, Sheng Y, Wu C. Antioxidation and mechanism of phosphites including the free phenolic hydroxyl group in polypropylene. J Appl Polym Sci, **134**, 44696 (2017). https://doi.org/10.1002/app.44696.

[3] Ying Q, Zhao Y, Liu Y. A study of thermal oxidative and thermal mechanical degradation of polypropylene. Makromol Chem Phys, **192**, 1041 (1991). https://doi.org/10.1002/macp.1991.021920503.

[4] Wang X, Wang B, Song L, Wen P, Tang G, Hu Y. Antioxidant behavior of a novel sulfur-bearing hindered phenolic antioxidant with a high molecular weight in polypropylene. Polym Degrad Stab, **98**, 1945 (2013). https://doi.org/10.1016/j.polymdegradstab.2013.05.019.

[5] Voigt W, Todesco R. New approaches to the melt stabilization of polyolefins. Polym Degrad Stab, **77**, 397 (2002). https://doi.org/10.1016/s0141-3910(02)00089-7.

[6] Richaud E, Fayolle B, Verdu J. Polypropylene stabilization by hindered phenols-kinetic aspects. Polym Degrad Stab, **96**, 1 (2011). https://doi.org/10.1016/j.polymdegradstab.2010.11.011.

[7] Allen NS, Edge M. Fundamentals of Polymer Degradation and Stabilization, 3rd ed., Elsevier, London, 22 (1992).

[8] Chen J, Yang MS, Zhang SM. Immobilization of antioxidant on nanosilica and the aging resistance behavior in polypropylene. Compos Part A Appl Sci Manuf, **42**, 471 (2011). https://doi.org/10.1016/j.compositesa.2011.01.006.

[9] Gadioli R, Morais JA, Waldman WR, De Paoli MA. The role of lignin in polypropylene composites with semi-bleached cellulose fibers: mechanical properties and its activity as antioxidant. Polym Degrad Stab, **108**, 23 (2014). https://doi.org/10.1016/j.polymdegradstab.2014.06.005.

[10] Zhang Q, Jiao Q, Leroux F, Tang P, Li D, Feng Y. Antioxidant intercalated hydrocalumite as multifunction nanofiller for Poly(propylene): synthesis, thermal stability, light stability, and anti-migration property. Polym Degrad Stab, **140**, 9 (2017). https://doi.org/10.1016/j.polymdegradstab.2017.04.012.

[11] Shi X, Wang J, Jiang B, Yang Y. Hindered phenol grafted carbon nanotubes for enhanced thermal oxidative stability of polyethylene. Polymer, **54**, 1167 (2013). https://doi.org/10.1016/j.polymer.2012.12.062.

[12] Jahanmardi R, Assempour H. Effects of galbanic acid on thermal and thermo-oxidative stabilities of LLDPE. Iran Polym J, **17**, 799 (2008).

[13] Karami N, Jahanmardi R. Evaluation of effects of thymolphthalein on thermooxidative stability of polypropylene. Polyolefins J, **4**, 79 (2017). https://doi.org/10.22063/POJ.2016.1394.

[14] Sabnis RW. Handbook of Acid-Base Indicators, CRC Press, Boca Raton, 361 (2007).

[15] Jahanmardi R, Pourattar P, Soleimani H, Shohani N. Effects of thymolphthalein on thermo-oxidative stability of high density polyethylene in melt and solid states. Iran J Chem Chem Eng, **36**, 39 (2017).

[16] Morrison RT, Boyd RN. Organic Chemistry, 6th ed., Pearson Education Inc., New Delhi, 585 (2002).

[17] Yuan B, Bao C, Qian X, Jiang S, Wen P, Xing W, Song L, Liew KM, Hu Y. Synergetic dispersion effect of graphene nanohybrid on the thermal stability and mechanical properties of ethylene vinyl acetate copolymer nanocomposite. Ind Eng Chem Res, **53**, 1143 (2011). https://doi.org/10.1021/ie403438k.

[18] Yuan B, Bao C, Song L, Hong N, Liew KM, Hu Y. Preparation of functionalized graphene oxide/polypropylene nanocomposite with significantly improved thermal stability and studies on the crystallization behavior and mechanical properties. Chem Eng J, **237**, 411 (2014). https://doi.org/10.1016/j.cej.2013.10.030.

[19] Tang XZ, Li W, Yu ZZ, Rafiee MA, Rafiee J, Yavari F, Koratkar N. Enhanced thermal stability in graphene oxide covalently functionalized with 2-amino-4,6-didodecylamino-1,3,5-triazine. Carbon, **49**, 1258 (2011). https://doi.org/10.1016/j.carbon.2010.11.044.

[20] Broska R, Rychly J, Csomorova K. Carboxylic acid assisted oxidation of polypropylene studied by chemiluminescence. Polym Degrad Stab, **63**, 231 (1999). https://doi.org/10.1016/s0141-3910(98)00097-4.

[21] Yang J, Huang Y, Lv Y, Zhao P, Yang Q, Li G. The intrinsic thermal-oxidative stabilization effect of chemically reduced graphene oxide on polypropylene. J Mater Chem A, **1**, 11184 (2013). https://doi.org/10.1039/c3ta11989k.