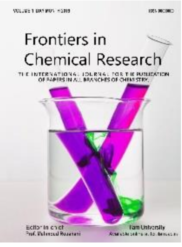

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Research article

Preparation of thymolphthalein stearate and appraisement of its efficacy as an antioxidant for polypropylene

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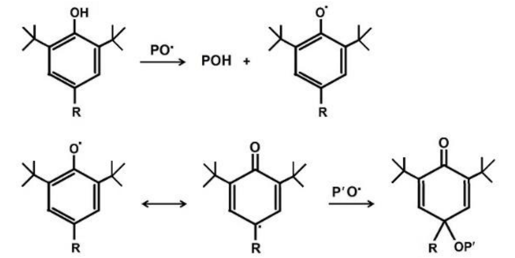
Abstract Stabilization of polypropylene (PP) against thermal oxidation during its melt processing and service life, due to its susceptibility to oxidation, is of great importance from both scientific and industrial points of view. The present work was devoted to synthesize a new antioxidant for polypropylene through esterification reaction between thymolphthalein and stearic acid. The occurrence of the reaction was confirmed by Fourier transform infrared (FT-IR) spectroscopy, size exclusion chromatography and melting point measurements. The reaction product was proved to be a mixture of thymolphthalein mono- and di-stearate. It was also shown that the esterification of thymolphthalein, in addition to lowering its polarity, lessens its melting point significantly from 246 to 186 °C, hence, helping the synthesized additive to be mixed with the polymer more favorably in comparison to thymolphthalein. Differential scanning calorimetry demonstrated that the new additive improves stability of the polymer in melt state, significantly. Moreover, oven ageing experiments revealed that the additive stabilizes the polymer against oxidation outstandingly in solid state and its efficiency is comparable to that of SONGNOX 1010, which is a powerful commercially used antioxidant for the polymer.

Keywords: Infrared spectroscopy; Polymer; Thermal oxidation; Thermo-oxidative stabilization.

1. Introduction

Polypropylene (PP), due to its excellent mechanical properties, chemical inertness, prominent processability and low price, is widely used in various applications, such as automotive parts, packaging, textiles, architectural materials etc. [1-3]. However, the presence of a labile 3º hydrogen atom in each repeating unit of its chain molecules, makes it susceptible to oxidative degradation [4]. Thermo-oxidative degradation (or thermal oxidation) during its high temperature melt processing as well as its service life is the most general kind of oxidative degradation, which is experienced by the polymer. Molecular structure of PP changes due to thermal oxidation via a free radical chain reaction, which eventually produces diverse oxidation groups such as acids, ketones, and so forth [5, 6]. However, the most undesirable outcome of the degradation is the reduction of molecular weight, which is signified by brittleness of the polymer artifacts [7]. Therefore, over the past decades a great deal of research work has been dedicated to thermo-oxidative stabilization of the polymer [5]. The stabilization is currently attained via the addition of antioxidants, which are incorporated into the polymer with a concentration of 0.05-1.0 wt.%. Two types of these particular stabilizers are currently being used: first, primary antioxidants, which deactivate free radicals present in the oxidation reactions and second, secondary antioxidants, which decompose hydro-peroxides, formation of which during the oxidation can lead to breakage of the chain molecules [8].

A widely used family of the primary antioxidants for PP is hindered phenols group, role of which is the suitable stabilization of the polymer during both melt processing and service life through donating a labile phenolic hydrogen atom to the free radicals according to a generally admitted stabilization mechanism shown in Scheme 1 [9-11]. However, the usage of these efficient antioxidants is associated with some significant concerns, e.g. abandoning the polymer via diffusion of their molecules from bulk of the polymer to its surface, which dwindles the concentration of antioxidant, thus, decreases its stabilization efficiency [12]. In addition, transformation of their molecules to colored compounds as a result of their stabilization reactions, can lead to some problems, particularly, in transparent artifacts [11]. So, over the past years, a large number of scientific efforts have been devoted to find new efficient antioxidants for the polymer with less deficiencies. Accordingly, efficiency of hyper-branched antioxidants and antioxidant-grafted polymers and nanoparticles in thermo-oxidative stabilization of polymer have been studied [13-15].



Scheme 1. Generally accepted mechanism for the stabilization action of phenolic antioxidants [9].

In a recent study, influence of 3,3-bis(4-hydroxy-2-methyl-5-propan-2-ylphenyl)-2-benzofuran-1-one, usually known as thymolphthalein having a molecular structure shown in Scheme 1, on thermo-oxidative stability of PP was investigated [16]. It was observed that thymolphthalein improves thermo-oxidative stability of the polymer eminently in both solid and melt states and its stabilization efficiency is comparable to that of SONGNOX 1010, a powerful commercially used phenolic antioxidant.

Furthermore, in another research work, it was proved that two allylic 3º hydrogen atoms of thymolphthalein molecule, which are specified in Scheme 2 by dashed circles, play the main role in its stabilization action and its phenolic hydrogen atoms don't have a considerable contribution in the stabilization reactions [17]. Accordingly, a mechanism for the stabilization action of thymolphthalein was proposed, which is depicted in Scheme 3.

However, thymolphthalein, owing to its small size as well as its low solubility in PP, which is due to dissimilar polarities of the polymer and the additive, is anticipated to have a high tendency to migrate from the bulk of the polymer [4]. This undesirable phenomenon can diminish its long-term stabilization performance. Therefore, the present work aimed at modifying the molecular structure of thymolphthalein, so that, it becomes less polar as well as bulkier.

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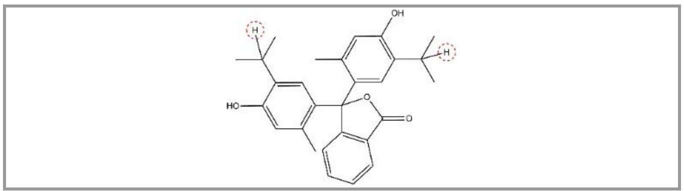
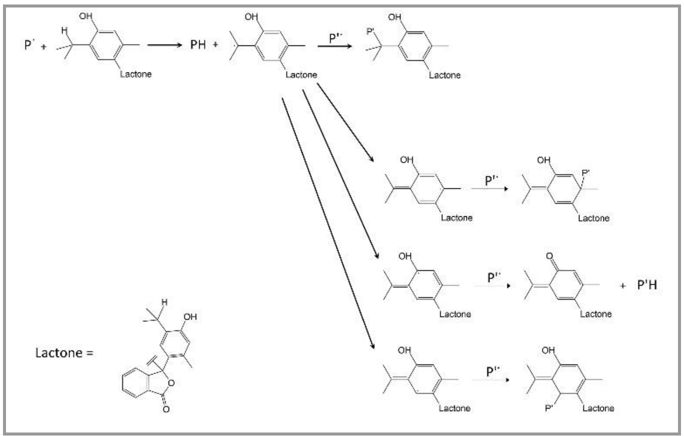


Scheme 2. Molecular structure of thymolphthalein [17].



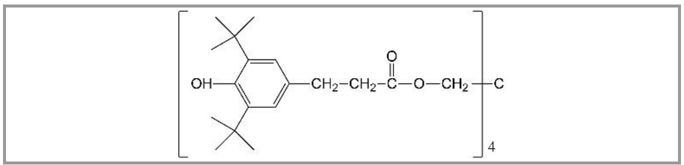
Scheme 3. Postulated reactions, through which thymolphthalein deactivates free radicals during its thermo-oxidative stabilization action [17].

The adopted strategy to achieve the goal was attaching a long non-polar hydrocarbon chain to molecular structure of thymolphthalein through an esterification reaction between its phenolic groups and carboxylic acid group of stearic acid. In this article, the success of the designed synthesis is illustrated by the results of Fourier transform infrared (FT-IR) spectroscopy, size exclusion chromatography (SEC) and melting point measurements. Moreover, efficiency of the modified antioxidant in stabilization of PP in molten and solid-states is reported based on the results of differential scanning calorimetry (DSC) and oven ageing experiments, respectively.

2. Experimental

2.1. Materials

Jampılen HP510M grade homopolymer PP with melt flow index (MFI) of 9.0 g/10 min, melting point of 167°C and density of 0.90 g/cm^3 containing 3000 ppm of Irganox 1010 as antioxidant was kindly supplied by Jam Petrochemical Company (Iran). SONGNOX 1010 phenolic antioxidant with the molecular structure shown in Scheme 4 was prepared as a white powder from Songwon Company (South Korea). Thymolphthalein, stearic acid and all other chemicals used in the esterification reaction, i.e., thionyl chloride, toluene, tetrahydrofuran (THF), dimethylformamide (DMF) and pyridine, were purchased, as synthesis grade, from Merck KGaA (Germany) and used as received.



Scheme 4. Molecular structure of SONGNOX 1010 [17].

2.1. General procedure for the synthesis of Antioxidant

2 g of the stearic acid was dissolved in a minimum amount of THF at ambient temperature using a magnetic stirrer. Then, the stearic acid solution was added slowly to 30 mL of thionyl chloride into a twin-neck flask. Subsequently, 0.4 mL of DMF was added as catalyst to the solution and kept at 70°C for 24 hours under reflux. Afterwards, thionyl chloride and THF were removed by reduced pressure distillation for 10 minutes, so that, a thick brownish liquid was left at the bottom of the flask. The remaining thick liquid, which was expected to contain stearoyl chloride, was dissolved immediately in 50 mL of toluene at ambient temperature. Subsequently, 1.52 g of thymolphthalein, which was already dissolved in 50 mL of toluene at ambient temperature, was added to the stearoyl chloride solution. Also, 0.4 mL of pyridine was added to the final solution in order to catalyze the reaction and neutralize the released hydrogen chloride in the reaction [4]. The obtained red solution was kept under reflux for 4 days. Afterwards, through complete evaporation of the solvent by heating at 80°C under vacuum, a pale brown sediment was obtained. In order to purify the material, the powder was washed several times by warm distilled water. This action, in addition to removing the unreacted thymolphthalein, also makes unreacted stearoyl chloride to be converted to stearic acid. Then, to remove the residual stearic acid, the resulting material was dissolved in a minimum amount of methanol at 60°C and by placing the solution container in a mixture of water and ice, stearic acid as a white powder was separated from the solution. This stage was repeated several times. Finally, the remaining solution was filtered and after complete evaporation of the solvent, the final product was obtained as an off-white powder.

2.3. Preparation of polymer film samples

In order to mix the polymer with the synthesized additive, according to the formulation of each sample, a certain amount of the additive was added to the molten polymer at 190°C in a Brabender internal mixer during 6 minutes at rotor speed of 60 rpm. Then, each prepared mixture was converted to a thin film with a thickness of 200 ± 20 µm, using a laboratory hot press at 190°C under a pressure of 20 MPa within 10 minutes. Also, for the sake of comparison, a blank sample without any additive, a sample containing an extra 0.2 wt.% of the commercial antioxidant, SONGNOX 1010, and a sample containing both of the additives, each having concentration of 0.2 wt.%, were prepared with the mentioned procedure. The formulations of the prepared film samples are presented in Table 1.

Table 1. Formulations of the prepared PP samples.

Sample designation	Blank	S2	T2	T5	T10	T2/S2
PP (wt. %)	100	99.8	99.8	99.5	99	99.6
SONGNOX 1010 (wt. %)	-	0.2	-	-	-	0.2
Thymolphthalein stearate (wt. %)	-	-	0.2	0.5	1.0	0.2

2.4. Characterization of the synthesized additive

In order to characterize the synthesized material, FT-IR spectroscopy, size exclusion chromatography (SEC) and melting point measurements were performed. To take FT-IR spectra of the product, a Thermo Nicolet FT-IR spectrophotometer (USA) was used. The spectra were obtained as average of 16 scans at a resolution of 4 cm^{-1} in the range of 4000 to 400 cm^{-1}. In order to perform SEC experiments, a Shimadzu LC-9A model instrument (Japan) was used. At first, three standard polystyrene (PS) samples with mono-dispersed molecular weight distribution and number-average molecular weight of 580, 1060 and 1700 Da, respectively, were used to calibrate the machine. Then, to perform chromatography experiments, a dilute solution of the synthesized product in THF solvent was injected into a chromatographic column, which was filled by porous PS gels using a syringe. The moving phase was THF and it was injected into the chromatographic column at 30°C with a flow rate of 1 mm/min. Finally, based on the sample elution time, its approximate molecular weight was calculated. To measure the melting point of raw materials and the product, a Krüss KSP1N model machine (Germany) was used. Heating rate was 1°C/min and three samples were tested for each of the materials and result was reported as average of the measured values.

2.4.1. Appraisement of thermo-oxidative stability of the samples in molten state

In order to study thermo-oxidative stability of the prepared samples in molten state, their oxidative induction time (OIT) and oxidation onset temperature (OOT) were measured using a Spico differential scanning calorimeter (DSC) (Iran).

Determination of oxidative induction time (OIT)

In this test, which was carried out according to ASTM D 3895, each polymer sample with a mass of about 10 mg was heated from ambient temperature to 200°C at a heating rate of 20 °C/min under a nitrogen atmosphere with a flow rate of 50 cm3/min. Then, at an isothermal condition, the nitrogen stream was replaced by an oxygen stream with the same flow rate. The time interval from the introduction of oxygen to onset of exothermic oxidation peak was recorded as OIT.

2.4.2. Determination of oxidation onset temperature (OOT)

This test was also performed using DSC machine in accordance with ASTM E 2009. Each polymer sample with a mass of about 10 mg was heated from 25°C to 300°C at a heating rate of 10 °C/min under oxygen atmosphere with a flow rate of 50 cm3/min. OOT was recorded as the temperature at which the DSC curve of the sample deviates from the flat line (base line) after the melting peak.

2.4.3. Appraisement of thermo-oxidative stability of the samples in solid state

To evaluate thermo-oxidative stability of the prepared film samples in solid state, thermal aging test was used. In this test, 4×4 cm2 pieces of the film samples were placed in an air-draft oven at 90°C for 4200 hours (25 weeks). The samples were taken out from the oven at several time intervals after being placed in the oven and were examined by FT-IR spectroscopy to assess the extent of their chemical changes during thermal oxidation. To take FT-IR spectra, the aforementioned spectrophotometer was used and the spectra were obtained as aver¬age of 16 scans at a resolution of 4 cm^{-1} in the wavenumber range of 4000–400 cm^{-1}. In order to measure the rate of oxidation in each sample during the aging test, rate of formation of carbonyl groups was assessed through determination of change of carbonyl index (ΔCI) at different time intervals using the following equation [18]:

$$\Delta CI = CI - CI_0 = \frac{A\,(1710)}{A\,(899)} - CI_0 \qquad \textbf{(1)}$$

In the above equation, CI and CI0 are carbonyl indices after and before degradation, respectively, and A represents the amount of absorbance at the wavenumbers specified in parentheses. Also, the wavenumbers of 1710 cm^{-1} and 899 cm^{-1} correspond, respectively, to carbonyl absorption peak and the reference peak. The latter was used as an internal thickness band to minimize the er-rors originating from the sample thickness [19].

3. Results and discussion

3.1. Characterization of the synthesized additive

In this work, we tried to synthesize thymolphthalein stearate in order to provide a new antioxidant with less polarity and molecular weight higher than that of thymolphthalein, in order to increase the probability of desirable uniform distribution of the additive throughout the polymer matrix and to reduce the possibility of migration from bulk of the polymer during its service life, respectively. Hence, it has to be proved that thymolphthalein stearate has been successfully synthesized. Then, its efficacy in stabilization of the polymer against thermal oxidation during its melt processing and also, long term weathering during its service life should be verified.

The occurrence of the esterification reaction was investigated using FT-IR spectroscopy, SEC and melting point measurements, the results of which are presented below.

FT-IR spectra were taken to unveil the changes that had occurred in molecular structure of the raw materials during the reaction. The taken FT-IR spectra are illustrated in Figure 1. In the spectrum of stearic acid, two absorption bands at wavenumbers of 2925 and 2850 cm^{-1} are seen, which are assigned to stretching vibration of aliphatic C-H bond [20-22]. These two absorption bands are also present in the spectrum of the product indicating presence of the aliphatic part of stearic acid molecule in the molecular structure of the product. Moreover, a strong and broad absorption band at 1696 cm^{-1} and a broad absorption band at 934 cm^{-1} are seen in the spectrum of stearic acid, which are related to stretching vibration of carboxylic carbonyl group and bending vibration of carboxylic hydroxyl group, respectively. These two bands are absent in the spectrum of the product, which implies consumption of the carboxylic acid group of stearic acid during the esterification reaction.

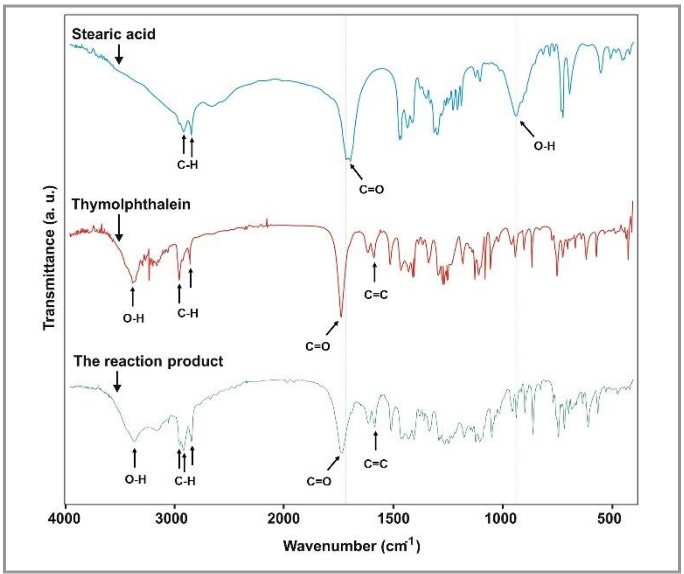
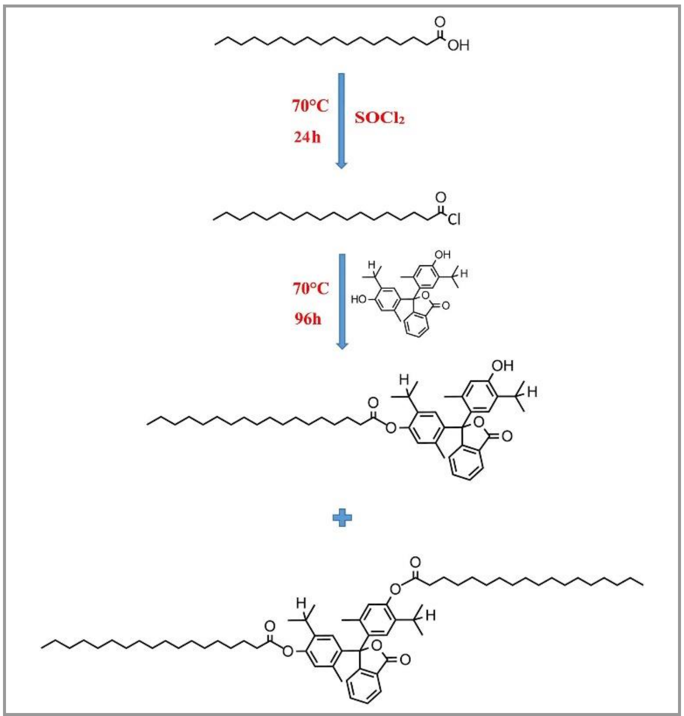


Figure 1. FT-IR spectra of stearic acid, thymolphthalein and the

reaction product.

Also, in the FT-IR spectrum of thymolphthalein there are several absorption bands, most notably are those at wavenumbers of 3377, 2960, 1737 and 1611 cm^{-1}, which are attributed to stretching vibrations of phenolic O-H bond, aliphatic C-H bond, esteric carbonyl group and aromatic C=C bond, respectively. These absorption bands are present in the spectrum of the synthesis product. However, two notable differences are seen between the spectra of the product and thymolphthalein: first, the absorption band of esteric carbonyl group is broader in the spectrum of the product, which can be due to the presence of two types of carbonyl groups in the molecular structure of the product, i.e. the one present in lactonic ring of thymolphthalein and that formed by the esterification reaction. The second difference is intensity of the peak of the phenolic O-H group at 3377 cm^{-1}, which is significantly lower in the spectrum of thymolphthalein in comparison to that of the product. This can be ascribed to partial consumption of the phenolic O-H groups of thymolphthalein during the esterification reaction with stearic acid as shown in Figure 2 [4].



Scheme 4. Schematic representation of the chemical reactions in the two-step esterification reaction between thymolphthalein and stearic acid.

In SEC technique different molecules present in a sample are isolated according to their size, thus, it can be possible to determine different molecular species in a sample as well as their abundance [23]. So, the reaction product was subjected to SEC in order to discover the number of different molecular species present in the product and to measure their molecular weights. The chromatogram taken from the reaction product is shown in Figure 3. In the graph the relative concentration of eluted molecules is illustrated in terms of elution time in the chromatography column. Only two overlapping peaks are seen in the chromatograph, which indicates that there are just two species with slightly different molecular sizes in the product. The right-hand peak corresponds to a species with smaller molecules, while the left-hand peak represents a specie with larger molecules. It is due to the fact that bulkier molecules in comparison to smaller molecules have lower accessibility to the pores of the porous gels of the chromatographic column and, hence, their elution time is shorter [23]. Therefore, calibration of the SEC column, using reference samples, allows to determine the approximate molecular weight of the components of a sample based on their elution time in the chromatographic column.

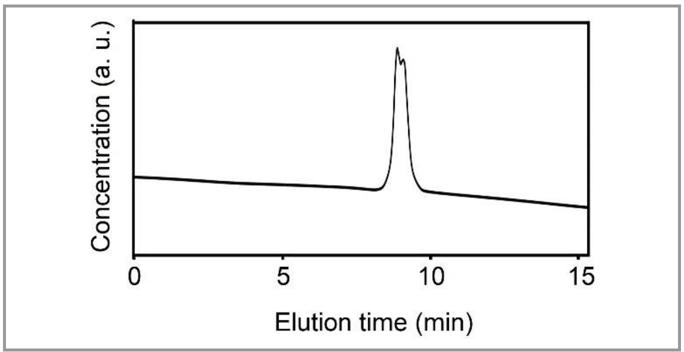


Figure 3. SEC Chromatogram of the reaction product.

According to the calibration curve of the column, the observed peaks in the chromatograph correspond to molecular weights of about 710 and 1000 kDa, respectively. On the other hand, the esterification reaction between thymolphthalein and stearic acid with molecular weights of 430 and 284 Da, respectively, is expected to yield two products, namely, a mono- and a di-ester with molecular weights of 696 Da and 962 Da, respectively. As actual molecular weight of both of thymolphthalein mono- and di-stearate are close to one of the values obtained by SEC, one can inferred that the both species are present in the product. The small differences between the actual and the measured molecular weights are due to the difference in the molecular structure of the tested product and the standard samples used for calibration of the SEC column.

Melting point of small molecules depends on their intermolecular forces and molecular weight. Hence, a change in either of these factors for a certain material can affect its melting point. On the other hand, it is necessary for a low-molecular-weight compound, which is aimed to be used as an additive for a polymer, to have a melting point lower than the melt processing temperature of the polymer. This is because small-molecule additives in their molten state can be better distributed throughout the molten polymer matrix in comparison to their solid state. Therefore, measurements of the raw materials and the reaction product was carried out in this work to further investigate the occurrence of the reaction as well as to check the suitability of the melting temperature of the additive. The measured melting point of the raw materials and the reaction product are shown in the Table 2. As it is seen, the melting point of the product is significantly different from that of the both raw materials, so that, it is 60°C less than the melting point of thymolphthalein and 115°C higher than the melting temperature of stearic acid. This remarkable difference cannot be explained in terms of simple mixing of thymolphthalein and stearic acid as they have significant polarities and hence, show poor miscibility. Therefore, the observation verifies the occurrence of the chemical reaction between thymolphthalein and stearic acid. In fact, by replacing one or both phenolic groups of thymolphthalein with the stearate base, its polarity and, consequently, its molecular interactions have been severely impaired, resulting in a significant reduction in its melting point.

Table 2. Results of melting point measurements.

Material	Melting point (°C) concentration
Stearic acid	Stearic acid
Thymolphthalein	Thymolphthalein
The reaction product	The reaction product

On the other hand, conventional processing temperature of PP, depending on the processing technique, is between 190-230°C. It is seen that the melting point of the reaction product (186°C) is less than the lower limit of the range of the polymer processing temperature, and thus, under the processing conditions, the reaction product is in molten state. Therefore, from the viewpoint of the availability of suitable mixing conditions, the use of this material as an additive for PP is possible.

According to the results of FT-IR spectroscopy, SEC and melting point measurements, one can conclude that the thymolphthalein stearate was successfully obtained via the reaction between thymolphthalein and stearic acid, though the product is a mixture of mono- and di-stearate esters. After proving the successful synthesis of thymolphthalein stearate, it is necessary to evaluate its anticipated effect on polymer stabilization against thermal oxidation. Therefore, various PP samples containing different concentrations of the additive was prepared and their thermo-oxidative stability in both melt and solid states was studied. Moreover, the stabilization efficiency of the additive was compared with that of the commercial phenolic antioxidant, Songnox 1010. In the following, the results of the thermal oxidation studies in melt and solid states are presented, respectively.

2.4.4. Appraisement of thermo-oxidative stability of the samples in molten state

Thermal oxidation of PP is an exothermic reaction so, its occurrence can be simply discovered by calorimetric methods. Therefore, to evaluate the thermo-oxidative stability of the samples in molten state, oxidation induction time (OIT) and oxidation onset temperature (OOT) of the samples were determined using differential scanning calorimetry (DSC). OIT and OOT are two known criteria for investigating the stability of polymers, in particular, polyolefins, against thermo-oxidative degradation in melt state [4, 24]. The DSC curves of the samples obtained from the isothermal (OIT) and the heat-ramp (OOT) tests are shown in Figures 4 and 5, respectively.

The time interval between the exposure to oxygen atmosphere and the commencement of the exothermic reaction (the deviation from the baseline), which is equivalent to OIT, is indicated in Figure 4 for all the samples. As can be seen in Figure 5, the indicated time period increases by the addition of either of thymolphthalein stearate or Songnox 1010 to the polymer, denoting the ability of the additives in thermo-oxidative stabilization of the polymer in melt state. However, it seems that the efficacy of the commercial antioxidant in the stabilization of the higher than the synthesized additive. It is also seen that the sample having both of the additives has an extremely high stability against the thermal oxidation. So, thymolphthalein stearate not doesn't interfere with the stabilization action of Songnox 1010, but also, elevates its efficiency.

In order to compare OIT values of different samples detailedly, the exact OIT values of the samples are presented in Table 3. It is seen that in the presence of thymolphthalein stearate OIT value of PP is increased steadily by augmenting concentration of the additive. OIT value of a given polymer is anticipated to be proportional to concentration of added antioxidant [23]. However, from the data presented in Table 3, one can infer that the amount of improvement in OIT for the samples containing thymolphthalein stearate is less sensitive to the concentration of the additive than is expected. A similar observation was reported for thermo-oxidative stabilization of PP by thymolphthalein [16]. In that study thymolphthalein with concentrations ranging from 0.1 to 1.0 wt. % was shown to elevate OIT of the polymer to a steady value of around 13 minutes. The phenomenon was explained in terms of poor distribution of the additive in the polymer, for which two reasons was proposed: first, the additive remains solid during the melt mixing with the polymer because of the fact that melting point of thymolphthalein is above the processing temperature of the polymer and second, low solubility of thymolphthalein in PP, which is due to their dissimilar polarities.

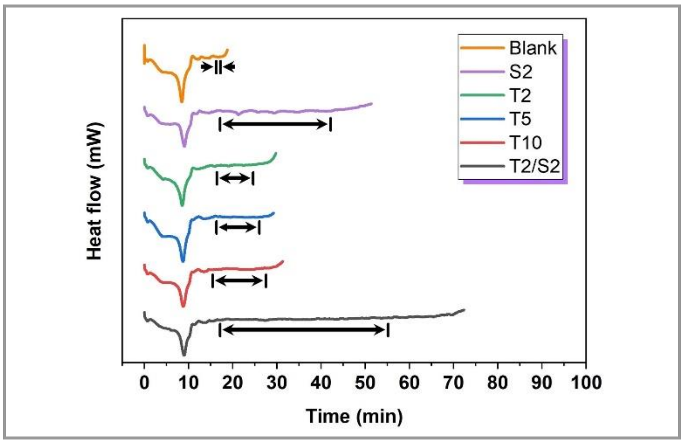


Figure 4. DSC curves of the PP samples obtained from OIT test.

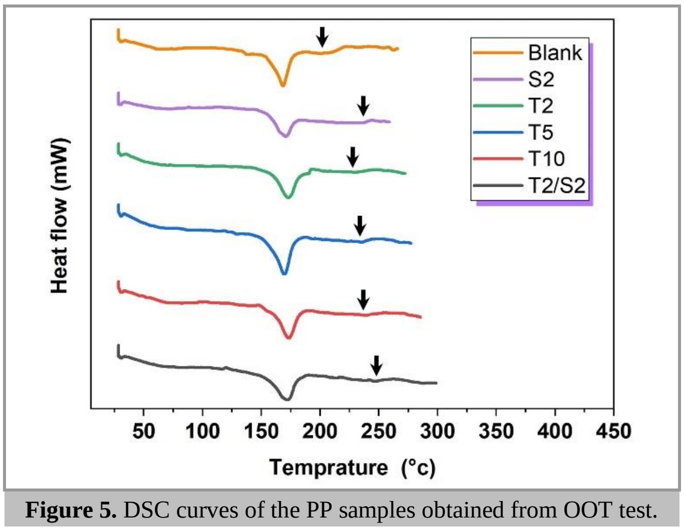


Figure 5. DSC curves of the PP samples obtained from OOT test.

Table 3. OIT and OOT values of the PP samples..

Sample designation	Blank	S2	T2	T5	T10	T2/S2
OIT (min)	1.7	25.1	8.8	9.6	12.1	37.7
OOT (°C)	201	238	229	234	237	249
OIT (min)	1.7	25.1	8.8	9.6	12.1	37.7

However, in this work OIT values in the presence of different amounts of thymolphthalein stearate are not similar and shows a somewhat weak dependence on the concentration of the additive. The difference can be ascribed to the better distribution of the additive in the polymer owing to the following two modifications which have occurred in the structure of thymolphthalein due to the reaction with stearic acid. First, melting point has fallen considerably, so that, thymolphthalein stearate is in molten state at the mixing temperature. Second, polarity and thus, strength of cohesive forces between molecules of the additive have diminished due to the replacement of phenolic hydroxyl group by low-polarity stearate group, which allows more facile separation of the additive molecules and their eventual better distribution. Despite the mentioned modifications, amount of improvements in OIT value in the presence of thymolphthalein stearate is slightly lower in comparison to thymolphthalein. This is because molecular weights of thymolphthalein mono- and di-stearate are, respectively, 62 and 124% higher than thymolphthalein. Thus, thymolphthalein, at a certain amount, has higher number of the main stabilizing group (i.e. benzylic 3º hydrogen atom) than thymolphthalein stearate and hence, is expected to exhibit more pronounced stabilization efficiency. Another probable reason for the phenomenon is the fact that phenolic hydrogen atoms of thymolphthalein, which slightly participate in the stabilization of the polymer, have been partially or completely removed through esterification reaction [17]. However, the stabilization efficacy of thymolphthalein is not remarkably higher than the other additive due to its undesirable distribution in the polymer.

On the other hand, none of the samples containing thymolphthalein stearate show OIT value as high as the sample containing Songnox 1010, which indicates some higher efficiency of the commercial antioxidant in the stabilization of the polymer in the molten state in comparison to thymolphthalein stearates. However, in the case of T2/S2 sample, which contains the both additives, an interesting result is seen, i.e. the OIT value of the sample is about 12 minutes higher than that of S2 sample containing only Songnox 1010. The obtained result, which is a valuable achievement, means that thymolphthalein stearate not only does not interfere with the stabilization role of the commercial antioxidant, but also improves it significantly. Similar synergistic effects between thymolphthalein and the 1010 antioxidant were reported in the case of OIT of PP and PE, respectively [16, 17]. The phenomenon was attributed to the similar stabilization mechanism of the both additives, i.e. playing the role of a chain-breaking-donor antioxidant in polymer. The hypothesis might be extended to the stabilization role of thymolphthalein stearate since the stearate group does not play any role in the stabilization mechanism.

In the heat-ramp (OOT) test, a broad exothermic peak after the melting peak in the DSC curve is assigned to thermal oxidation [24]. Therefore, the temperature corresponding to the onset of the oxidation peak (OOT), which is indicated in Figure 5 for all the samples, is considered as a criterion for thermo-oxidative stability in melt state. As it can be seen in Figure 5, the addition of 0.2-1.0 wt.% of thymolphthalein stearate to the polymer, in the case of T2, T5 and T10 samples, shifts the oxidation onset to higher temperatures implying, again, the stabilization role of thymolphthalein stearate. In order to assess the stabilization efficiency of the additives more precisely, OOT values of all the samples are illustrated in Table 3. Similar to the results of the OIT test, it is observed that increasing the concentration of thymolphthalein stearates from 0.0 wt.% (in Blank sample) to 1 wt.% (in T10 sample) elevates OOT value steadily from 201 to 237°C. Unlike the OIT results, OOT values of the samples containing thymolphthalein stearate are comparable to that of S2 sample containing Songnox 1010. This means that the stabilization effect of thymolphthalein stearate becomes more profound by increasing temperature. The phenomenon can be attributed to better distribution and higher mobility of the additive at higher temperatures, because the melting points of the additive and the polymer are close to each other and they both melt nearly simultaneously, hence, the additive molecules can freely move in the molten polymer matrix. The effect was not reported in the case of thymolphthalein, which might be due to the fact that the oxidation of the samples commenced before melting of the additive at 246°C. At the testing conditions, thymolphthalein molecules do not have desired mobility in the polymer, so, the additive does not have the opportunity to be blended appropriately with the polymer [16].

Here, in the case of T2/S2 sample containing 0.2 wt. % of each of Songnox 1010 and thymolphthalein stearate, a synergistic effect can be seen again, since the OOT value of the sample is noticeably higher than that of S2 and T2 samples containing 0.2 wt. % of either of the two additives, respectively. Similar results were reported when studying effects of thymolphthalein and the 1010 antioxidant on OOT of PP and PE, which suggested the analogous chain-breaking-donor roles of the 1010 antioxidant and thymolphthalein in the polymer [16, 17].

As a whole, it can be deduced that thymolphthalein stearate have a significant antioxidant activity in PP in molten state. However, its efficiency in the stabilization of the polymer is not quite as outstanding as the commercially used phenolic antioxidant, Songnox 1010.

2.4.5. Appraisement of thermo-oxidative stability of the samples in solid state

Due to thermo-oxidative degradation of polypropylene, several chemical groups are formed on the polymer chains, including carbonyl and hydroxyl groups, the formation of which can be traced by FT-IR spectroscopy [25, 26]. The fact that the absorption band of carbonyl groups appears in the wavenumber range of 1840-1650 cm^{-1}, where other chemical groups do not show any absorption peak, has led researchers to examine appearance and evolution of carbonyl absorption band in FT-IR spectrum of the polymer to study kinetics of its thermal oxidation. Therefore, in this study, FT-IR spectroscopy was applied to compare rate of thermal oxidation of different film samples subjected to oven ageing at 90°C. FT-IR spectra taken from Blank and T2 samples after being aged for different times, are shown in Figures 6 and 7, respectively. In these spectra characteristic absorption bands of PP, i.e., stretching vibration of C-H bonds belonging to the methyl, methylene and methenyl groups, in the range of 2957 to 2841 cm^{-1}, bending vibration of the C-H bonds at 1458 and 1375 cm^{-1}, bending vibration of isopropyl group at 1167 cm^{-1} and out-of-plane bending of C-H bonds in different terminal vinyl groups at wavenumbers of 997, 972, 899, 840 and 808 cm^{-1} are observed [20]. Moreover, it is seen in Figure 6 that the carbonyl absorption peak has appeared in the FT-IR spectrum of Blank sample after 1344 hours (8 weeks) of aging at 90°C. However, spectra in Fig 7 do not show formation of carbonyl groups in T2 sample even after 2856 hours (17 weeks) of aging. The observed difference between the two samples demonstrates the profound stabilizing effect of thymolphthalein stearate on the thermal oxidation of the polymer in solid state. It should be noted that the initial weak absorptions in the carbonyl region of the FT-IR spectra of the two samples belong to the carbonyl groups present in molecular structure of the antioxidant, which was already contained in the polymer.

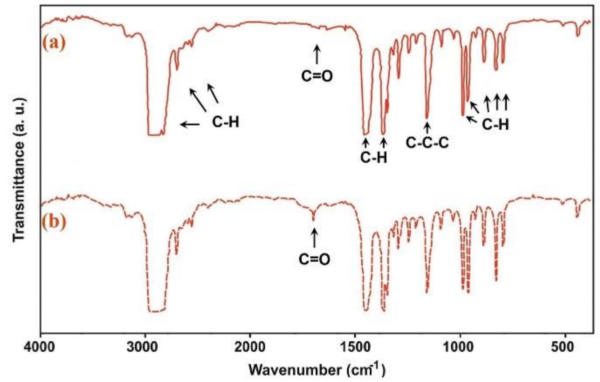


Figure 6. FTIR spectra of Blank sample (a) before and (b) after oven aging at 90°C for 1344 hours (8 weeks).

In order to reach a more vivid assessment of the stability of the samples against thermal oxidation in oven ageing experiment, amounts of ΔCI of the tested samples for various ageing durations were calculated using equation (1) and are illustrated in Figure 7.

As it can be seen, ΔCI of each samples remains zero for an individual period, during which the polymer resists against thermal oxidation [27].

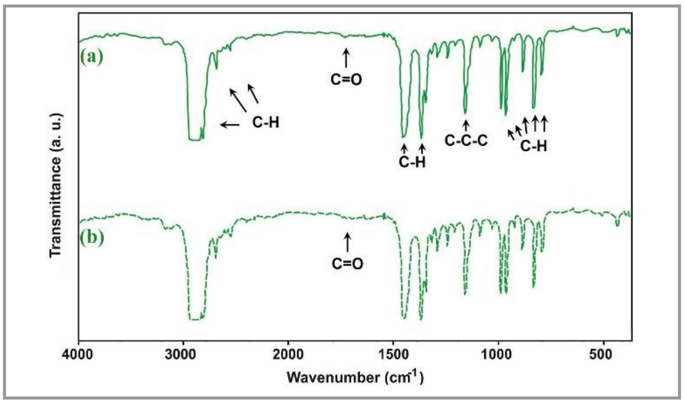


Figure 6. FT-IR spectra of T2 sample (a) before and (b) after oven aging at 90°C for 2856 hours (17 weeks).

Accordingly, the length of this induction period for each sample signifies its thermo-oxidative stability. It is observed that induction period of the polymer has been extended from about 500 h (in the case of Blank sample) to around 2800 and 3000 h through addition of 0.2 wt. % of thymolphthalein stearate (in the case of T2 sample) and Songnox 1010 (in the case of S2 sample), respectively. In other words, thymolphthalein stearate and Songnox 1010 at the same concentration of 0.2 wt. % have amended the thermo-oxidative stability of the polymer dramatically and the amounts of the modification are almost similar. It was reported that in oven ageing experiment at 90°C thymolphthalein with concentrations of 0.1-1.0 wt. % extended induction period of PP from about 500 h to more than 1800 h [16]. However, the exact amount of the modified induction time was not reported as the duration of the ageing test was only 1800 h. A similar activity for thymolphthalein was also reported in the ageing of HDPE [17].

It is also seen in Figure 7 that the samples T5, T10 and T2/S2 do not show any growth in ΔCI up to 4200 h (25 weeks) indicating their extraordinary stability against the oxidation in solid state. Here, the synergism between thymolphthalein stearate and Songnox 1010 is observed as the induction period of T2/S2 containing the both additives at the same concentration of 0.2 wt. %, is much higher than the induction periods of T2 and S2 samples having 0.2 wt. % of either of the additives.

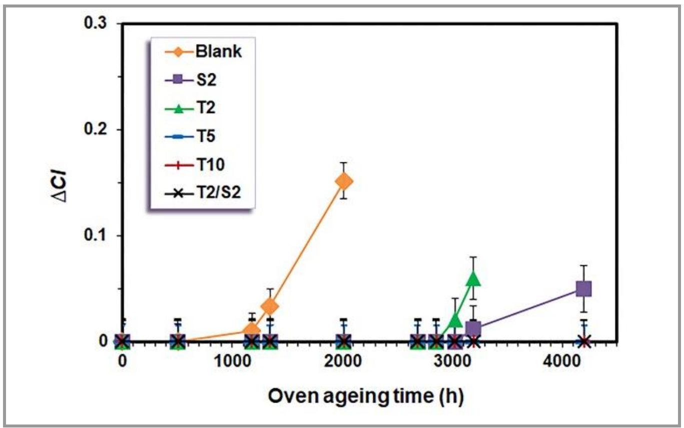


Figure 7. Change of carbonyl index (ΔCI) for the film samples as a function of time of oven aging at 90°C

The better performance of thymolphthalein stearate in solid state than in melt state can be assigned to the fact that the oxidation in solid state is much slower than in melt state, hence, the additive molecules have enough time to reach free radicals in the polymer and play their role as radical scavenger. However, in melt state, due to higher rate of oxidation reactions, the additive molecules have a limited opportunity to reach the harmful free radicals and react with them. In these circumstances Songnox 1010 molecules show higher efficiency, which may be due to their better distribution in the polymer, better mobility, higher number of stabilizing groups per antioxidant molecule or faster reaction with the free radicals.

Conclusion

Stabilization of PP for desirable melt processing and also service life, due to its poor resistance against thermal oxidation, has been an important field of study in polymer science and technology for years. As a straightforward route to achieve the mentioned goal antioxidants are being used. In this study, successful synthesis of thymolphthalein stearate, as a new antioxidant for PP, with relatively bulky and non-polar molecules, which hinders its gradual migration from the polymer, was reported. It was shown that, the prepared additive, have a tremendous ability in thermo-oxidative stabilization of PP in solid state, so that, its performance is similar to that of the commercially used phenolic antioxidant, Songnox1010. Thus, depending on its concentration, it can extend service life of the polymer artifacts to a proper amount. The new additive was also demonstrated to stabilize the polymer against thermal oxidation in the molten state noticeably. So, it has the ability to enhance safety of the polymer in melt processing. However, in this case, the performance of the additive is somewhat lower in comparison to Songnox1010. Finally, due to the observed synergism between thymolphthalein stearate and Songnox1010 in the thermo-oxidative stabilization of polypropylene in both solid and melt states, the two additives can be used together for the stabilization of the polymer.

References

[1] T. Jiang, C. Liu, L. Liu, J. Hong, M. Dong, X. Deng, RSC Adv., 6 (2016) 91720.

[2] P. Monji, R. Jahanmardi, M. Mehranpour, Carbon Lett., 27 (2018) 81.

[3] M. Shahvazian, M. Ghaffari, H. Azimi, R. Jahanmardi, Int. Nano Lett., 2 (2012) 27.

[4] M. Bagheripour-Asl, R. Jahanmardi, H. Tahermansouri, E. Forghani, Carbon Lett., 25 (2018) 60.

[5] D. Bertin, M. Leblanc, S. R. A. Marque, D. Siri, Polym. Degrad. Stab., 95 (2010) 782.

[6] X. Meng, Z. Jiang, Z. Xin, W. Chen, Y. Sheng, C. Wu., J. Appl. Polym. Sci., 134 (2017) 44696.

[7] Q. Ying, Y. Zhao, Y. Liu., Makromol. Chem., 192 (1991) 1041.

[8] X. Wang, B. Wang, L. Song, P. Wen, G. Tang, Y. Hua., Polym. Degrad. Stab., 98 (2013) 1945.

[9] W. Voigt, R. Todesco, Polym. Degrad. Stab., 77 (2002) 397.

[10] E. Richaud, B. Fayolle, J. Verdu, Polym. Degrad. Stab., 96 (2011) 1.

[11] N. S. Allen, M. Edge, Fundamentals of polymer degradation and stabilization, Elsevier, London, 1992.

[12] J. Chen, M. S. Yang, S. M. Zhang, Composites: Part A, 42 (2011) 471.

[13] G. Kasza, T. Stumphauser, A. Nádor, Z. Osváth, G. Szarka, A. Domján, J. Mosnáček, B. Iván, Polymer, 124 (2016) 210.

[14] A. Manteghi, S. Ahmadi, H. Arabi, Polym. Degrad. Stab., 138 (2018) 41.

[15] J. Bu, X. Huang, S. Li, P. Jiang, Carbon, 106 (2016) 218.

[16] N. Karami, R. Jahanmardi, Polyolefins J., 4 (2017) 79.

[17] R. Jahanmardi, P. Pourattar, H. Soleimani, N. Shohani, Iran. J. Chem. Chem. Eng., 36 (2017) 39.

[18] N. Chavoshi, R. Jahanmardi, Fuller. Nanotub. Car. N., 27 (2019) 1.

[19] R. Jahanmardi, H. Assempour, e-Polymers, 8 (2008) 156.

[20] R. T. Morrison, R. N. Boyd, Organic chemistry, Prentice-Hall, New Jersey, 1992.

[21] H. A. Raslan, E. S. Fathy, R. M. Mohamed, Int. J. Polym. Anal. Ch., 23 (2018) 181.

[22] V. M. Riechert, A. G. Ferrofino, J. A. Ressia, M. D. Failla ,L. M. Quinzani, Int. J. Polym. Anal. Ch., 24 (2019) 353.

[23] U. W. Gedde, Polymer Physics, Chapman & Hall, London, 1995.

[24] W. W. Focke, I. van der Westhuizen, J. Therm. Anal. Calorim., 99 (2019) 285.

[25] B. Eyheraguibel, M. Leremboure, M. Traikia, M. Sancelme, S. Bonhomme, D. Fromageot, J. Lemaire, J. Lacoste, and A. M. Delort, Chemosphere, 198 (2018) 182.

[26] F. Portillo, O. Yashchuk, É. Hermida, Polym. Test., 53 (2016) 58.

[27] Ammala, A., S. Bateman, K. Dean, E. Petinakis, P. Sangwan, S. Wong, Q. Yuan, L. Yu, C. Patrick, K. H. Leong, Prog. Polym. Sci., 36 (2011) 1015.

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