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Preparation of a new polymeric antioxidant for polypropylene based on phenylmalonic acid

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Abstract Stabilization of polypropylene (PP) against thermal oxidation, due to the susceptibility of this commodity polymer to oxidation, is of great importance from both scientific and industrial points of view. The present work aimed at preparing a new polymeric antioxidant for polypropylene, which has no tendency toward migration from the polymer. Accordingly, a diacid (phenylmalonic acid), which has a labile hydrogen atom and can act as a hydrogen donor antioxidant, was polymerized with 1,4-phenylenediamine to render a polyamide. Occurrence of the reaction was confirmed by FT-IR spectroscopy, differential scanning calorimetry (DSC), gel permeation chromatography and thermogravimetric analysis (TGA). The synthesized polyamide was melt-mixed with PP and its uniform distribution in the matrix was verified by the yellowness index measurements. Oxidation onset temperature and oxidative induction time of the samples using DSC proved that the additive enhances stability of the polymer remarkably in melt state. However, its stabilization efficiency is not as outstanding as that of SONGNOX 1010; a conventional antioxidant for PP. But oven ageing experiments followed by FT-IR spectroscopy revealed that the synthesized antioxidant amends thermo-oxidative stability of the polymer in solid state with an eminent efficiency which is even better than that of SONGNOX 1010. Furthermore, its remarkable stabilization activity was proved by DPPH method. Finally, the synthesized polyamide's potential, as an efficient antioxidant for PP, especially in the long-term stabilization, was assigned to the presence of the two different hydrogen donor groups, i.e. allylic and amine hydrogen atoms, in the molecular structure of the new antioxidant.

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

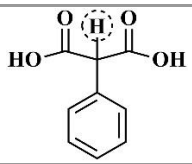
1. Introduction

The stabilization of polymeric materials is of paramount importance, first of all, from the point of view of the dynamically developing polymer industry [1]. Ageing of polymeric materials, due to their oxidation, is widespread and poses serious problems because the occurrence of oxidation, even at limited extent, can cause irreversible and damaging changes in their physical and mechanical properties [2-4]. The degradation, ageing and stabilization of polymers constitute a considerable area of interest in industry as well as science of polymers, and the aim is to obtain new, stable polymeric materials [5]. Polypropylene (PP) is widely used for various purposes. It is a typical semi-crystalline thermoplastic polymer derived from the propylene olefin monomer. Since being discovered in 1954, PP has quickly become one of the most popular commodity plastics due to its chemical inertness, prominent processability, low density and low cost with desirable mechanical properties [6-9]. Molecular structure of PP, because of the presence of a labile 30 hydrogen atom in each repeating unit of its chain molecules, makes it susceptible to oxidative degradation [10]. For this reason, PP requires an addition of proper antioxidants for every stage of its lifecycle [11].

Unfortunately, the polymers are subjected to heat and shearing forces during processing, and they are exposed to oxygen, light, heat, and water during their service life [12]. All of these factors cause oxidative degradation of the polymer, which results in undesirable changes in chemical, physical, mechanical and appearance characteristics. Formation of alkyl radical (R•) and alkyl peroxyl radical (ROO•) are of key importance during the degradation. The worst feature of the process is the production of hydroperoxide (ROOH), which decomposes into two additional active radicals [11, 13]. To avoid the polymer oxidative degradation, antioxidants are added to polymers in small amounts, which either interfere with propagation of R• and ROO• radicals or deactivate ROOH species [14-16]. Accordingly, antioxidants can be divided into two broad classes, that is, primary and secondary antioxidants, depending on their mode of action. The primary antioxidants break the degradation chain by donating H-atoms to free radicals, which is formed during polymer degradation, thus preventing those radicals from propagating the chain reaction [17-19]. The secondary antioxidants, on the other hand, hamper the oxidation reaction through transformation of the hydroperoxides to inert species, such as alcohols [20, 21].

One of the most important primary antioxidants are hindered phenols and alkyl aryl amines. SONGNOX 1010, as a commercial phenolic antioxidant with low molecular weight, have poor compatibility and long-term stability in non-polar polymers, e.g. PP, and can easily migrate to the surface of these polymers, which limit their application [22]. Hence, their stabilization efficiency may decline during service life of the polymer products. Thus, during recent years, a great deal of research work has been devoted to make antioxidant molecules bulkier in order to prevent their migration, which, in turn, leads in smaller changes in their efficiency during service life of polymers [23].

On the other hand, it has been shown that the presence of 3° allylic hydrogen atom in a chemical compound donates thermo-oxidative stabilization capability to the compound [10, 24, 25]. Hence, in order to prepare a new high molecular weight antioxidant for PP, in the present work, we tried to polymerize phenylmalonic acid (PMA) having 3° allylic hydrogen atom in its molecular structure (Scheme 1) with 1,4-phenylenediamine (PD) to yield a polyamide. Accordingly, the success of the designed synthesis is illustrated by the results of Fourier transform infrared (FT-IR) spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Furthermore, efficiency of the synthesized polymeric compound in stabilization of PP in molten and solid-states is reported based on the results of DSC and oven ageing experiments, respectively. Moreover, antioxidant activity of the new compound was also assessed by 2,2-diphenyl-1-picrylhydrazyl (DPPH) method and its ability to be distributed in the polymer uniformly as well as its effect on the polymer's color were also assessed by Yellowness Index (YI) determination.



Scheme 1. Molecular structure of PMA [26].

2. Experimental

2.1. Materials

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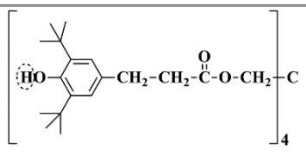
The used PP (HP510 grade) with MFI of 9.0 g/10 min and melting point of 167°C was obtained from Jam Petrochemical Company (Iran). Phenylmalonic acid (PMA) with purity of 98% and melting point of 153-155°C and 1,4-phenylenediamine (PD) were purchased from Sigma-Aldrich. SONGNOX 1010, as a commercially used phenolic antioxidant, was prepared as white powder from Songwon Company (South Korea). The molecular structure of SONGNOX 1010 with its specified active groups is shown in Scheme 2.

All other chemicals used in the synthesis, i.e., dichloromethane, tetrahydrofuran (THF) and methanol were purchased from Merck kGaA (Germany) and used as received. DPPH and butylated hydroxytoluene (BHT) were obtain from Sigma-Aldrich for radical scavenging test.



Scheme 2. Molecular structure of SONGNOX 1010 [23].

2.2. Antioxidant synthesis.

11 mmol of PD was dissolved in 40 mL of THF, at ambient temperature using a magnetic stirrer. Then, 10 mmol of PMA was added to the solution and stirred for 72 hours, at 360 rpm. Direct synthesis method was adopted because of high reactivity of the diamide with the diacid. At the end of the polymerization, the solvent was evaporated and the residue was washed with dichloromethane and distilled water, respectively and, then, it was dried in a vacuum oven at 50°C to obtain a pale brown powder.

2.3. Preparation of polymer film samples

In order to mix the polymer with the synthesized additive, in accordance to the formulation of each sample, a certain amount of the synthesized polyamide was added to the molten polymer at 190°C in a Brabender internal mixer during 6 minutes at a 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. Moreover, for comparison, a blank sample without any additive and a sample containing 0.1 wt. % of SONGNOX 1010 were prepared according to the mentioned procedure. The formulations of the prepared film samples are presented in Table 1.

2.4. Characterization of the synthesized additive

For structural characterization of the synthesized polyamide (PA), FTIR spectroscopy using a Thermo Nicolet FTIR spectrophotometer (USA) was used. The spectra were obtained as an average of 16 scans at a resolution of 4 cm^{-1} in the range of 4000 to 400 cm^{-1}. Thermal behavior of the new additive was evaluated using a DuPont 910 DSC thermal analysis system (USA). About 10 mg of either of PMA or PA was heated from 25°C to 350°C at a heating rate of 10°C/min under air atmosphere with a flow rate of 50 mL/min. GPC using Shimadzu LC-20A instrument equipped with Styrogel HR2 column (ASTM D5296) was applied to measure molecular weight of the synthesis product. The solvent and the moving phase were both THF and the experiments were carried out at 30°C with a flow rate of 1 mL/min. Molecular weight was calculated according to a universal calibration curve, which was drawn using different standard polystyrene (PS) samples with mono-dispersed molecular weight distribution. To determine the thermal stability of the samples at high temperatures a Netzsch 209 F1 model TGA analyzer (Germany) was used. For TGA experiments, samples of about 5 mg weight were heated from 20°C to 600°C at a constant heating rate of 10 °C/min under a stream of nitrogen with a flow rate of 50 mL/min.

Table 1. Formulation of the prepared PP film samples.

Sample designation	Blank	PMA-1	PMA-2	PA-2	S-1
PP (wt. %)	100	99.9	99.8	99.8	99.9
Phenylmalonic acid (PMA) (wt. %)	-	0.1	0.2	-	-
Synthesized Polyamide (PA) (wt. %)	-	-	-	0.2	-
SONGNOX 1010 (wt. %)	-	-	-	-	0.1
PP (wt. %)	100	99.9	99.8	99.8	99.9

2.5. Determination of Yellowness Index

YI is a spectrophotometric index, which can be used to describe any change in color of a material due to addition of an additive [27, 28]. On the other hand, the final test results are the average of different points on the film, so it is possible to investigate the quality of the additive distribution in the film samples through the evaluation of standard deviation of the data. Measurements of color characteristics were performed using a HunterLab UltraScan VIS model instrument (USA). The data in this test are values of the main color parameters of the samples (L: the amount of brightness from zero (black) to 100 (white), a: -60 (green) to +60 (red) and b: -60 (blue) to +60 (yellow)), which can be obtained from measuring 5 different points of the film (one of them at the center and four at the periphery) and averaging them. By comparing the parameters with the reference (Blank), other information such as total color difference (ΔE) and YI are calculated using the following Equations:

$$\Delta L = L_{ref} - L_{sample} \quad (1)$$

$$\Delta a = a_{ref} - a_{sample} \quad (2)$$

$$\Delta b = b_{ref} - b_{sample} \quad (3)$$

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (4)$$

$$YI = \frac{142.86\, b_{sample}}{L_{sample}} \quad (5)$$

Also, standard deviation (σ) of each L data series was calculated using Equation (6):

$$\sigma = \sqrt{\sum_{i=1}^{N=5} \frac{(L_i)^2}{N-1} - (\bar{L})^2} \quad (6)$$

Where, L_i and $\bar{L}$ are a data point from a series of L and average value of the series.

To measure the antioxidant activity of the PA and PMA, DPPH radical scavenging activity assay was used. The free radical method is an antioxidant assay based on electron-transfer that produces a violet solution in methanol. DPPH free radical, stable at room temperature, is reduced in the presence of an antioxidant molecule,

giving rise to colorless methanol solution according to a reaction demonstrated in Figure 1. The use of the DPPH assay provides an easy and rapid way to evaluate the antioxidant activity by UV-vis. spectrophotometry. As it can be seen in Figure 1, DPPH is a stable free radical that has an unpaired electron on one of its nitrogen atoms [29- 31]. The highest absorption is in the range of 515-520 nm. The reaction of DPPH• with antioxidants decreases the amount of DPPH• and its absorption. Consequently, antioxidant activity can be determined.

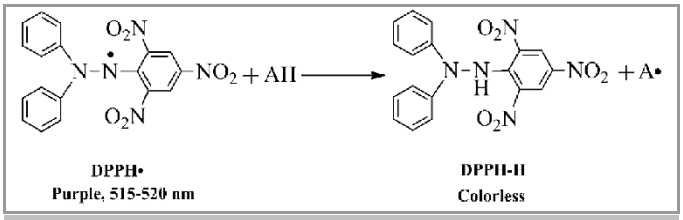


Figure 1. An illustration of the chemical reaction involved in the radical scavenging by DPPH [32].

By measuring the decrease in absorption intensity of DPPH solution using a DR5000 model Hach instrument (Canada) and expressing test results based on Radical Scavenging Activity (RSA%) using the Equation (7), the antioxidant activity can be evaluated:

$$RSA\% = \left(A_{Blank} - A_{Sample}\right) \div \left(A_{Blank}\right) \times 100 \qquad (7)$$

where, A_{Blank} and A_{sample} are the absorbance of the DPPH solution and the tested sample, respectively.
In order to do the experiment, different concentrations of each solution sample (0.01 to 0.04 wt. % solution of PA and PMA) were prepared, and 2 mL of each solution was added to 1 mL of 6 × 10-5 M DPPH• solution. The resulted solution was kept in a dark environment at room temperature for 20 minutes. Then, the absorbance of the solution was measured at 517 nm by the aforementioned UV-vis. spectrophotometer and RSA% was calculated according to the Equation (7). Finally, to compare the obtained results, Songnox1010 and BHT were used as standard antioxidants and their RSA% was calculated in a similar manner [33]. The steps are schematically illustrated in the Figure 2.

2.6. Appraisement of thermo-oxidative stability of the PP film samples in melt state

In order to study thermo-oxidative stability of the prepared film samples in molten state, their oxidative induction time (OIT) and oxidation onset temperature (OOT) were measured using the aforementioned DSC instrument.

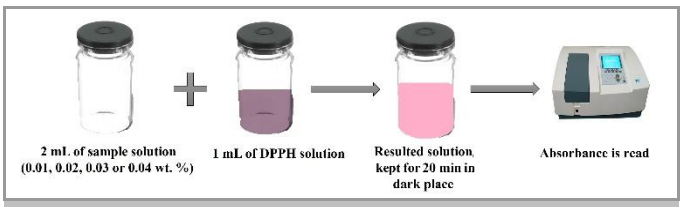


Figure 2. Schematic representation of antioxidant capacity determination by free radical scavenging.

2.7. 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 180°C at a heating rate of 20 °C/min under a nitrogen atmosphere with a flow rate of 50 mL/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.

2.8. Determination of oxidation onset temperature (OOT)

This test was also performed using the abovementioned DSC machine in accordance to ASTM E 2009. Each polymer sample with a mass of about 10 mg was heated from 25°C to 250°C at a heating rate of 10 °C/min under oxygen atmosphere with a flow rate of 50 mL/min. OOT was recorded as the temperature at which the DSC curve of the sample deviates from the base-line after the melting peak.

2.9. Appraisement of thermo-oxidative stability of the PP film samples in solid state

To evaluate thermo-oxidative stability of the prepared film samples in solid state, thermal aging test was performed. In this test, 4×4 cm pieces of the film samples were placed in an air-draft oven at 100°C for 1440 hours (8 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 average of 16 scans at a resolution of 4 cm-1 in the wavenumber range of 4000–400 cm-1. In order to measure 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 (8) [34]:

$$\Delta CI = CI - CI_0 = A_{1710}/A_{899} - CI_0 \qquad (8)$$

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 by subscripts. Also, the wavenumbers of 1710 and 899 cm-1 correspond, respectively, to carbonyl absorption peak and the reference peak, which was used as an internal thickness band to minimize the errors originating from the sample thickness [24].

3. Results and discussion

3.1. Characterization of the synthesized additive

In this work, we tried to synthesize a new polymeric antioxidant in order to hinder its migration from the polymer (PP). Moreover, it was tried to maintain compatibility of the antioxidant and the polymer through limiting the molecular weight of the additive, in order to increase the probability of the desirable uniform distribution of the additive throughout the polymer matrix. Hence, it has to be proved that polyamide antioxidant with the desired molecular weight (< 20 kDa) has been successfully synthesized. Then, its efficacy in stabilization of the polymer against thermal oxidation during its melting process and also, long term weathering during its service life should be verified. The occurrence of the polymerization reaction was investigated using FT-IR spectroscopy, DSC, GPC and TGA, the results of which are presented below.

FT-IR spectra make it possible to monitor changes that occur in molecular structure of raw materials during a chemical reaction. Figure 3 shows the infrared spectra of PMA (a), PD (b) and the reaction product (c). A characteristic broad absorption band related to the stretching vibration and a sharp peak related to the bending vibration of carboxylic OH group at 3500-2500 cm-1 and 934 cm-1, respectively, as well as a sharp absorption band due to stretching

vibration of carboxylic carbonyl group at 1702 cm-1 in the spectrum of PMA have been disappeared in the spectrum of the reaction product, which refers to the consumption of the mentioned group through the reaction. Furthermore, an absorption band at 1570 cm-1, which can be attributed to the bending vibration of NH bond of amide group, has been appeared in the spectrum of the reaction product indicating the formation of amide group [35, 36].
The possible reaction for step-growth of polymerization of PMA with PD and the synthesis of the polyamide additive are shown in Figure 4, in which, functional groups that are expected to have free radical scavenging activity, have been specified. It should be note that in addition to 3° allylic carbon atom, aryl amine groups are anticipated to show hydrogen donating activity, which results in deactivation of free radicals.

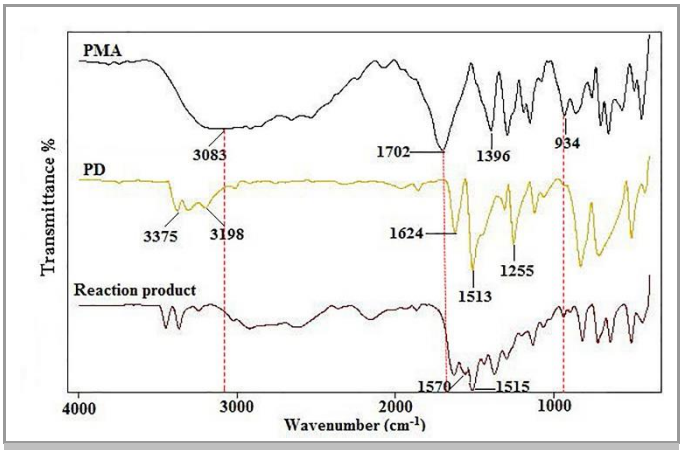


Figure 3. FT-IR spectra of PMA, PD and the reaction product.

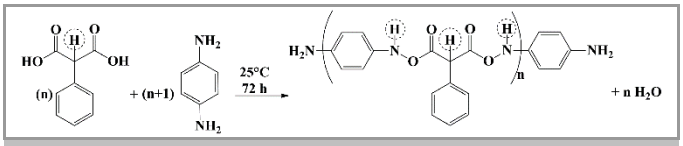


Figure 4. The step-growth polymerization of PMA and PD.

Change in either intermolecular forces and molecular weight for a certain material can affect its DSC curve. Thus, DSC was carried out on the raw materials and the reaction product to further investigate the occurrence of the reaction as well as to check whether melt blending of the additive with PP is possible, i.e. to examine whether the additive melts before melting of PP. The DSC curves of PMA and the reaction product are shown in Figure 5. It is also reported by Hyun-Seung Kim, Keon-Joon Leen and their colleagues that PD melts at 145°C showing a sharp melting peak [37]. Two adjacent melting peaks are seen in DSC curve of PMA at 153 and 178°C, relating to PMA and 1,3-phenylene diacetic acid, respectively [26,38,39]. The latter di-acid is formed during the production process of PMA as a by-product and cannot be removed from the final product. Nevertheless, as it has two carboxylic acid groups in its molecular structure, it can participate in the step-growth polymerization reaction with PMA and PD as a di-acid. On the other hand, DSC curve of the reaction product shows a sharp melting peak at 99°C. As the peak is located at a temperature which is far below the melting range of the three raw materials, it can be inferred that the reaction between PMA, PD and 1,3-phenylene diacetic acid has happened and the observed peak is due to the melting of the produced polyamide.
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 (99°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.

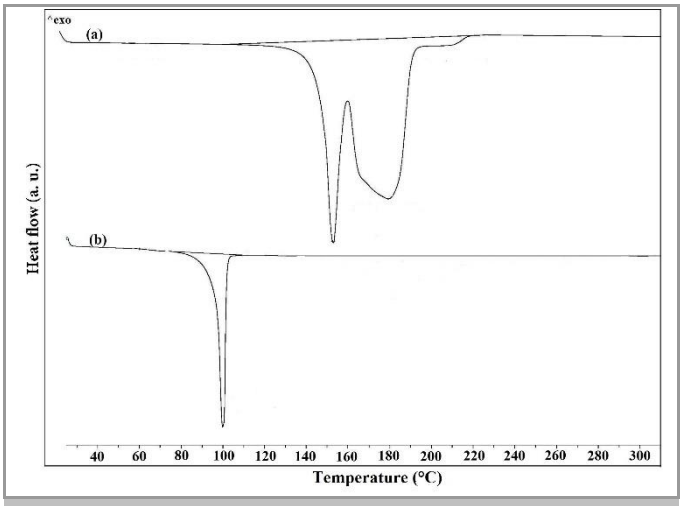


Figure 5. DSC curves related to purified a) PMA and b) PA.

GPC, which is also known as size exclusion chromatography (SEC), can determine molecular weight distribution and all of three average molecular weights of polymers i.e. number-, weight- and z-averages. Hence, in the present work the synthesized additive was subjected to GPC experiments to measure its molecular weight distribution and number-average molecular weight. Figure 6 exhibits the obtained chromatograph of the additive, which shows a narrow mono-modal molecular weight distribution. According to the obtained results, the number-average molecular weight of the reaction product is 19.4 kDa with PDI of 1.42, which is far higher than the molecular weights of the raw materials, 180, 108 and 194 Da for PMA, PD and 1,3-phenylene diacetic acid, respectively. This, in turn, proves the occurrence of polymerization reaction. The success in the polymerization reaction resulting in the production of PA can be assigned to the high reactivity of PD [40].

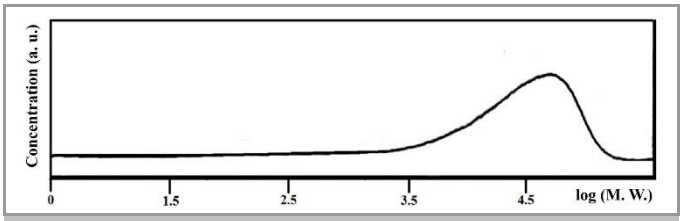


Figure 6. Gel permeation chromatogram of PA.

TGA is a useful analytical technique by which thermal behavior of materials, in particular their thermal stability, can be evaluated. TGA curves of PMA and PA are obtained from the analysis in nitrogen atmosphere and their derivative (DTG) curves are shown in Figure 7. It is seen in Figure 7-a that onset of weight loss happens at 140°C for both compounds. However, rate of weight loss for PA is considerably slower than that of PMA. Moreover, according to DTG curves, the temperature corresponding to maximum rate of weight loss of PA (210°C) is much higher than that of PMA (153°C). Finally, less than 1% of the initial weight of PMA remains at 210°C, whereas about 70% of PA is left at this temperature. These significant differences between thermal behaviors of the two compounds imply that a PA has undergone a chemical reaction, which modifies its thermal stability. The observed low thermal

stability of PMA can be assigned to its two carboxylic acid groups, which are believed to accelerate degradative reactions [1, 11, 41].

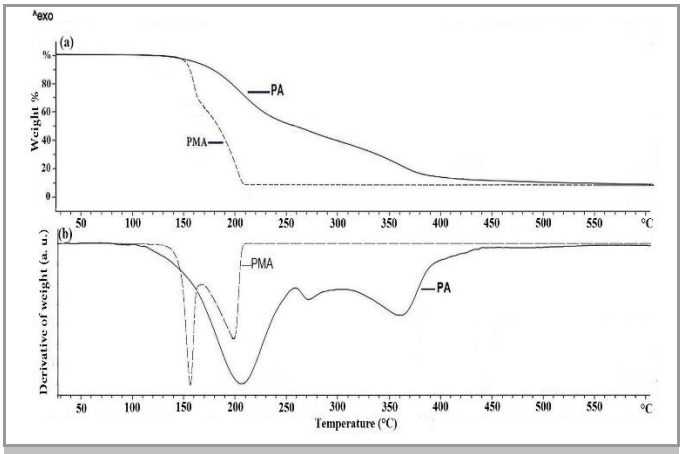


Figure 7. (a) TGA and (b) DTG curves of PA and PMA.

3.2. Evaluation of YI

YI measurements were carried out to check the state of distribution of the additives in the prepared samples and also to evaluate the extent of change in the polymer's color, which is caused by individual additives. The obtained results are illustrated in Table 2. Based on the results of the Hunter color parameters (a, b, L) obtained from 5 different locations of the films and standard deviation for L values, which are shown in Table 2, even distribution of the additives in all film samples are proven. Some negligible differences can be attributed to the slight differences in the film thickness. On the other hand, based on the results of the calculated YI and (ΔE) parameters of the films, the addition of each of PMA, PA or SONGNOX1010 changes the PP color indicators. However, the smallest amount of color change is in the case of PMA-2 sample and the highest one belongs to PA-2 sample. In general, due to the white color of PMA and SONGNOX1010 and pale brown color of the synthesized antioxidant, the obtained results were anticipated. Hence, the new additive, provided that proves its efficiency in thermal stabilization of the polymer, can be used in products that are intended to have relatively dark color.

3.3. Evaluation of antioxidant activity

The results of DPPH test on PMA and PA samples as well as SONGNOX 1010 and BHT as standard samples, based on the measured absorption and RSA% (percentage of radical scavenging activity) values calculated by Equation (7), are given in Table 3. It should be pointed out that the results of BHT are similar to those found in other studies, which can be an indication for the reliability of the experiment and the obtained data [33]. As mentioned before, in DPPH test, DPPH• reacts with the antioxidants diminishing its concentration, which causes a decrease in the absorbance at 517 nm. According to the information presented in Table 3, for all tested samples, rising concentration decreases the amount of absorbance and enhances the amount of RSA%. In addition, it can be said that the radical scavenging activity of PA is higher in comparison to Songnox1010 and BHT promising its antioxidant activity in PP. Also, RSA% of PMA, with values of about 77%, indicates antioxidant potential of this substance. As the two carboxylic acid groups present in molecular structure of PMA do not play stabilizing role, the observed radical scavenging behavior can only be attributed to its 3° allylic hydrogen atom. Moreover, the remarkably higher RSA% of PA compared with PMA can be due to the presence of hydrogen atoms of aryl amine functional groups, which have been proven to deactivate free radicals through hydrogen donating action [1, 42]. In the following, the anticipated stabilization activity of PA in PP film is investigated.

Table 2. The Hunter color parameters, transparency and YI of the film samples.

Films	L		a		b		σ (Standard deviation for L data)	ΔE	YI
	0	100	+60	-60	+60	-60			
Blank	39.225		0.395		-0.710		0.053	0	-2.59
PMA-2	39.000		0.393		-0.716		0.031	0.225	-2.62
PA-2	36.186		0.596		0.323		0.051	3.216	1.28
S-1	38.990		0.403		-0.683		0.072	0.237	-2.50

Table 3. Values of absorbance for PMA, PA, SONGNOX 1010 and BHT at different concentrations measured by spectrophotometer and their calculated RSA% values.

Sample	Concentration (g /dL)	Absorbance at 517 nm				RSA%		
		PMA	PA	SONGNOX1010	BHT	PMA	PA	SONGNOX1010
1	0.01	0.675	0.778	0.763	0.935	76.473	92.323	92.471
2	0.02	0.678	0.537	0.685	0.922	76.368	94.701	93.241
3	0.03	0.638	0.182	0.655	0.917	77.762	98.204	93.537
4	0.04	0.653	0.151	0.622	0.915	77.739	98.510	93.862

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

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 PA and PMA in stabilizing the PP against thermo-oxidative degradation in the melt state, both OOT and OIT values were measured separately for all the samples. The DSC curves of the samples obtained from the heat-ramp (OOT) test and the obtained OIT values are presented in Figures 8 and 9, respectively. It can be seen in Figures 8 and 9 that in both OOT and OIT tests, PA can promote stability of the polymer against thermal oxidation remarkably in melt state. However, as it can be seen in Figure 8, the addition of 0.2 wt. % of the synthesized polyamide elevates OOT of PP from 205°C (in the case of Blank sample) to 223°C (in the case of PA-2 sample). The result is similar to that obtained by the addition of 0.1 wt. % of SONGNOX 1010 (in the case of S-1 sample). As the concentration of the new antioxidant is twice as

much as that of SONGNOX 1010, it can be deduced that the stabilization efficiency of the new additive is not as outstanding as that of SONGNOX 1010. This may be due to the higher molecular mobility of the commercially used antioxidant, SONGNOX 1010. On the other hand, it is seen in Figure 9 that OIT value of PA-2 sample containing 0.2 wt. % of the synthesized polyamide is lower in comparison to S-1 sample, which again indicates that stabilization efficiency of SONGNOX 1010 is higher than that of the new antioxidant. Besides, according to OOT values obtained through addition of 0.2 wt. % of PMA, in the case of PMA-2 sample, which is 29°C lower than that of Blank sample, it can be inferred that the carboxylic acid groups of PMA has an adverse effect on the stability of PP. These groups were transformed to amide groups through reaction of PMA with PD and, hence, their unfavorable effects are not seen in the case of PA. Therefore, the remaining 3° allylic hydrogen atoms and, probably, the aryl amine groups, are responsible for the stabilization action of PA in PP.

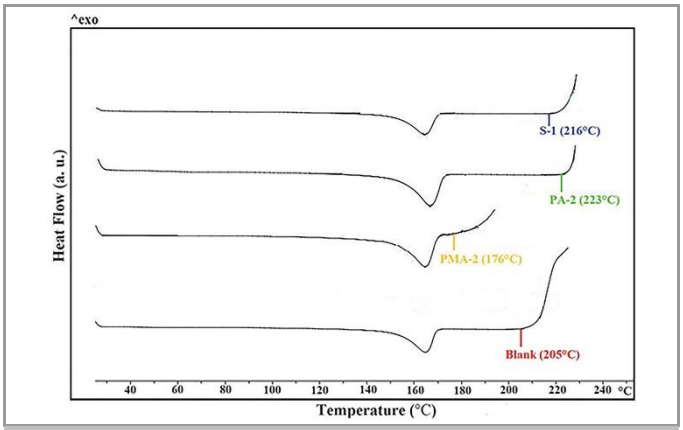


Figure 8. DSC curves of the PP samples obtained from OOT test.

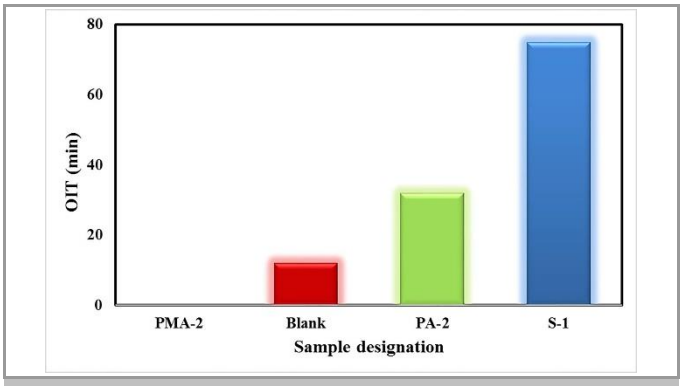


Figure 9. The values of OIT obtained for the samples.

3.5. 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 [43, 44]. 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 100°C. FT-IR spectra taken from Blank and PA-2 samples after being aged for different time intervals, are shown in Figures 10 and 11, respectively. As it is seen in Figure 10, the carbonyl absorption peak has appeared in the FT-IR spectrum of Blank sample after 60 days of aging at 100°C. However, spectra in Figure 11 do not show impressive formation of carbonyl groups in PA-2 sample after the same ageing time (60 days). The observed difference between the two samples demonstrates the profound stabilizing effect of the polyamide additive 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(s), which was/were already contained in the polymer [45, 46, 47].

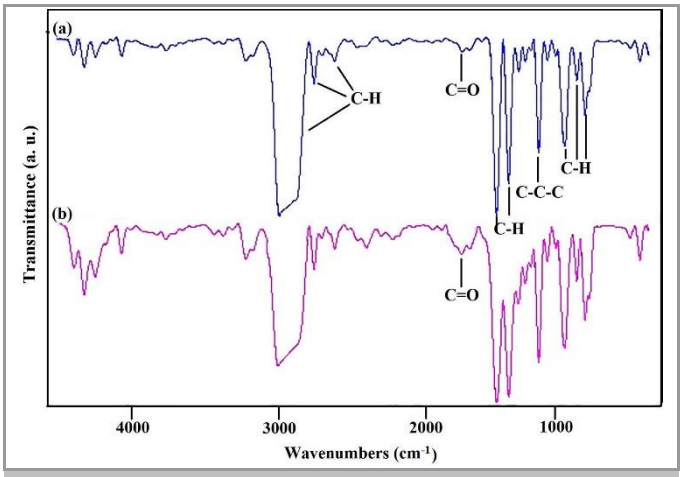


Figure 10. FT-IR spectra of Blank sample (a), before and (b) after oven aging at 100°C for 60 days.

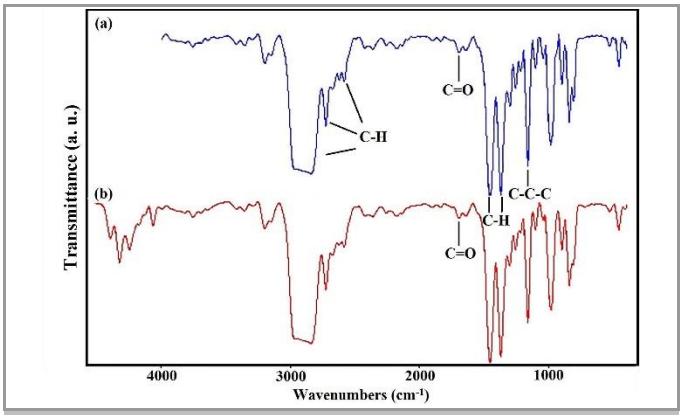


Figure 11. FT-IR spectra of PA-2 sample (a), before and (b) after oven aging at 100°C for 60 days.

In order to reach a more vivid assessment of the stability of the samples and clarify the efficiency of PA in stabilizing the polymer against thermal oxidation in oven ageing experiment, amounts of ΔCI of the tested samples for various ageing durations were calculated using Equation (8) and are illustrated in Figure 12. Intense increase of ΔCI for Blank and PMA-2 samples indicates extensive auto-oxidation of the polymer in these samples. On the other hand, slow increase in ΔCI are observed for the (PA-2 and S-1) samples. The growth of ΔCI for PA-2 sample during oven ageing is also slower compared to S-1 samples. It seems that more effective deactivation of free radicals by PA with allylic hydrogen atoms in solid state as well as the presence of active amid groups, together with higher concentration of antioxidant in PA-2 sample can be the reasons why PA-2 has a higher thermo-oxidative stability in solid state in comparison with S-1 sample. Also, the better performance of the polyamide antioxidant 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's bulky 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's molecules have a limited opportunity to reach the harmful free radicals and react with them.

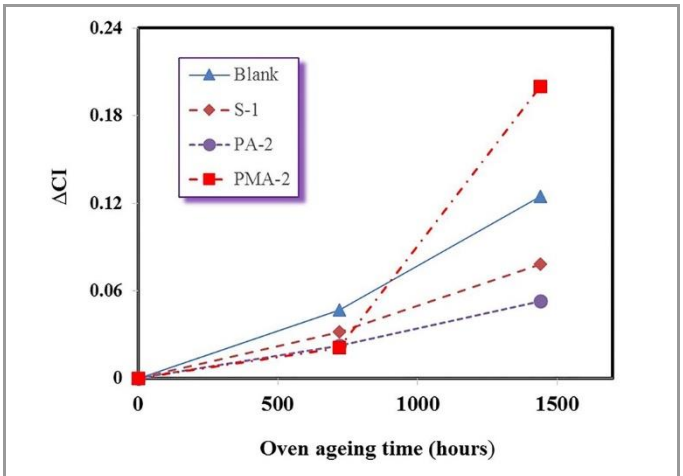


Figure 12. Change of carbonyl index (ΔCI) for the film samples as a function of time of oven aging at 100°C.

Conclusion

Successful synthesis of a polyamide antioxidant through a cost-effective, direct and catalyst-free step-growth polymerization using PA and PD as monomers was reported and attributed to high amine activity of PD. The prepared antioxidant was shown to have potential of enhancing thermo-oxidative stability of PP in both melt and solid states. Furthermore, relatively high molecular weight of the synthesized antioxidant can be an advantage due to hindrance against migration of antioxidant molecules from the polymer. Moreover, the presence of two active groups (amine and allylic hydrogen atoms) next to each other, makes synergistic effect on free radical scavenging.

The stabilization efficiency of the new antioxidant was shown to be better in solid state as compared to the melt state, which was attributed to the lack of need for high mobility of antioxidant molecules in solid state additive. Hence, this can feature it as a long-term thermo-oxidative stabilizer for PP rather than a fast high-temperature stabilizer for the polymer. On the other hand, it can also be predicted that the synthesized antioxidant can be more favorable in high-temperature stabilization of polymers such as polyethylene with lower processing temperatures, as compared to PP.

References

[1] H. Zweifel, Stabilization of polymeric materials, Springer, Berlin, 1998.

[2] S. Al-Malaika, Thermal antioxidants, Springer, Dordrecht, 1999.

[3] C.A. Albertsson, S. Karlsson, J. Appl. Polym. Sci., 35 (1988) 1289.

[4] Gahleitner M., Fiebig J., in: J. Karger-Kocsis (Ed.) Polypropylene. Polymer Science and Technology Series, Springer, Dordrecht, 1999.

[5] J. Fiebig, M. Gahleitner, C. Paulik, J. Wolfschwenger, Polymer Test., 18 (1999) 257.

[6] M.H. Hisham, Am. J. Polym. Sci., 6 (2016) 1.

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

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

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

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

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

[12] W.O. Drake, in: J. Edenbaum (Ed.), Plastics additives and modifiers handbook, Chapman and Hall, London, 1996.

[13] W. Schnabel, Polymer Degradation, Hanser, Munich, 1981.

[14] P. Mariani, G. Carianni, La. F.P. Mantia, Polym. Degrad. Stab., 85 (2004) 1003.

[15] E.B. Zeynalov, N.S. Allen, Polym. Degrad. Stab., 85 (2004) 847.

[16] J. Pospisil, Polym. Degrad. Stab., 20 (1988) 181.

[17] F. Eniko, L. Jan, Polym. Degrad. Stab., 66 (1999) 31.

[18] R. Axel, M. Elisabeth, S. Manfred, S. Affolter, Polym. Test., 24 (2005) 498.

[19] P.B Sulekha, Thesis from Cochin University, Department of Polymer Science, 2002.

[20] T. Zaharescu, S. Jipa, R. Setnescu, D. Wurm, M.J.S. Brites, M.A.F. Esteves, B. Marcelo-Curto, M.J. Gigante, Polym. Degrad. Stab., 68 (2000) 83.

[21] C. Li, J. Wang, M. Ning, H. Zhang, J. Appl. Polym. Sci., 124 (2011) 4127.

[22] I. Vulic, G. Vitarelli, J.M. Zenner, Polym. Degrad. Stab., 78 (2002) 27.

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

[24] R. Jahanmardi, H.Assempour, E-Polymers, 8 (2008) 156.

[25] R. Jahanmardi, M. Saberi, M. Fathi, N. Fazeli, 12th International Seminar on Polymer Science and Technology, Tehran, 2016.

[26] A.A. Morton, F. Fallwell, L. Palmer, J. Am. Chem. Soc., 60 (1938) 1426.

[27] N.K. Kortei, G.T. Odamtten, M. Obodai, V.Appiah, P.T. Akonor, Croat. J. Food Technol., Biotechnol. Nutr. 10 (2015) 66.

[28] P. Zapotoczny, A. Ratajski, M. Markowski, K. Majewska and H. Konopk, J. Food Eng., 76 (2004) 469.

[29] N. Jadid, D. Hidayati, S.R. Hartanti, B.A. Arraniry, R.Y. Rachman, Wiwi, AIP Conference Proceedings 1854, 020019, 2017. DOI: 10.1063/1.4985410.

[30] S. Trombino, R. Cassano, T. Ferarelli, Molecules, 17 (2012) 12734.

[31] T. Dizhbite, G. Telysheva, V. Jurkjane, U. Viesturs, Bioresour. Technol., 95 (2004) 309.

[32] N. Liang, D.D. Kitts, Molecules, 19 (2014) 19182.

[33] R. Mammadov, A. Makasçı-Afacan, D. Uysal–Demir, Iran. J. Chem. Chem. Eng., 29 (2010) 47.

[34] N. Chavoshi, R. Jahanmardi, Fuller. Nanotube. Car. N., 27 (2019) 1.

[35] D.A. Skoog, Principles of instrumental analysis, Saunders college publishing, New York, 1985.

[36] L. Barbeş, C. Rădulescu, C. Stihi, Rom Rep. Phys., 66 (2014) 765.

[37] H. Kim, K.J. Lee, Y.K. Han, J.H. Ryu, Seung M.oh, Sci.Dir. J. Power Sources, 348 (2017) 264.

[38] K. Miyamoto, H. Ohta, Biotechnol. Lett., 14 (1992) 363.

[39] M. Huhn, E. Somfai, G.Szabo, G. Resovszki, Z. Gneth, U.S. patent 4,289,894 , 1981.

[40] A. Meyer, K. Fischer, Environ. Sci. Eur., 27 (2015) 1.

[41] O. Novotný, K. Cejpek, J. Velíšek, Czech J. Food Sci., 26 (2007) 117.

[42] M. Soleimani, L. Dehabadi, L.D. Wilson, L.G. Tabil, in: D.W. Johnson (Ed.), Lubrication-tribology, lubricants and additives, Intech Open, London, 2018.

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

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

[45] N. Rouba, T. Sadoun, N. Boutagrabet, D. Kerrouche, S. Zadi, N. Mimi, Iran. J. Chem. Chem. Eng., 34 (2015) 69.

[46] J. Coates, in: R.A. Meyers, M.L. McKelvy (Eds.), Encyclopedia of Analytical Chemistry, Wiley, New York, 2006.

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

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