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Phenolic Antioxidant for Polyolefins from Grafted Phenol on Polyethylene Wax

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Summery: This study consists of the preparation of a new polymeric antioxidant from the grafting of phenol on the backbone of chlorinated polyethylene wax by alkylation's reaction in the presence of $AlCl_3$ as catalyst. The chemical structure of the prepared phenolic polyethylene wax(ph - wax) was characterized by FTIR. The thermal oxidation of HDPE was examined by monitoring the amount of O_2 uptake by samples of HDPE with the (ph-wax) volumetrically at 230 °C, also the thermal oxidation degradation of HDPE with the (ph-wax) derivative was studied by monitoring the weight loss of the samples during heating at 250 °C and under normal air as atmosphere. The results of this study show a decrease in the rate of HDPE oxidation in the presence of ph-wax at four percent (0.2, 0.4, 0.6 and 0.8) %wt/wt of polymer, while the oxidation time of HDPE increased from 5 min. for pure HDPE to reach 41 min. for (0.8) % sample. The thermograms and thermal data of this study indicate that the stability of HDPE increases with the percent of the (ph-wax) (0.6 and 0.8) wt/wt%. Generally, these results show that phenolic wax has excellent performance as an antioxidant for polyethylene.

Keywords: antioxidants; chlorinated wax; HDPE oxidation; phenolic wax; polymer oxidation

Introduction

Due to the wide-scale production of polymers throughout the world, the problem of their protection from degradation and oxidation during production and uses has become of great scientific and technological importance. Among the variety of polymers, polyethylene undergos oxidation – degradation by the oxygen of atmosphere which caused a fall in physico–mechanical properties that included a decrease in strength and elongation, change in resistively, colour changes, etc.[1–3] Therefore the addition of antioxidants to polyethylene or other commercial polymers is needed. Antioxidants are often small molecules with sites that can react with free radicals and hydroperoxides that are produced during oxidation reactions[4]; the effectiveness of all types of antioxidants is dependent on some factors such as the number of reactive groups, chemical structure, some physical properties, concentration of antioxidant and environmental factors.[5–9]

In general, the concentration of these additives decrease during long –term uses, many attempts have been made to solve this important problem, one of them is the use of high concentration of antioxidants or by bonding (grafted) it into polymer chains by chemical bonds or by using high molecular weight antioxidants.[1]

The purpose of this study was to synthesize and evaluate a grafted phenolic polyethylene wax as antioxidant for polyethylene.

Experimental Part

Chemicals

High density polyethylene (fluff) additive free grade M624 (MI = 6.0 gm/10 min. and density = 0.964 gm/cm^3), chlorine gas and

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polyethylene wax (as side product from low density polyethylene unit) were supplied by state company for petrochemical industries – Basrah-Iraq, polyethylene wax was used as crude without further purification. Other reagents such as AlCl3, were commercially obtained from Fluka. Nitrobenzene, CCl_4 and benzene were obtained from Aldrich. Oxygen gas was obtained from Basrah Gases Company with 99.5% purity.

Instruments

Infrared spectra were recorded by Fourier transform infrared spectrometer type (Shimatzu FTIR–4800s); Sartoriums AG Gutting electronic balance (with 0.1 mg accuracy) was used for monitoring the changes in the weight of samples, the apparatus that was used for monitoring the weight of sample illustrated in Figure 1. Oxidation measurements were determined out by oxygen uptake apparatus that described already described.[1,3]

Methods

Preparation of Chlorinated wax (Cl-wax)

Chlorinated polyethylene wax was prepared according to the method that was described in reference,[10] which consists of the reaction of polyethylene wax with chlorine in CCl_4 at 60 °C for 3 hr.

Preparation of Phenolic Polyethylene wax (ph-wax)

Ph-Wax derivative was obtained by alkylation reaction as follows: 4 g of anhydrous $AlCl_3$ was dissolved in 100 ml of nitrobenzene with stirring for 15 min, then 10 g of Cl-Wax was added to this solution with continuous stirring;after mixing the components well, the temperature was raised to 100 °C. 1 g phenol dissolved in nitrobenzene was added drop by drop for 15 min. The mixture was allowed to stand at 100 °C with stirring for 2 hr. The phenolic polyethylene wax was filtered and washed with benzene many times then dried at 100 °C.

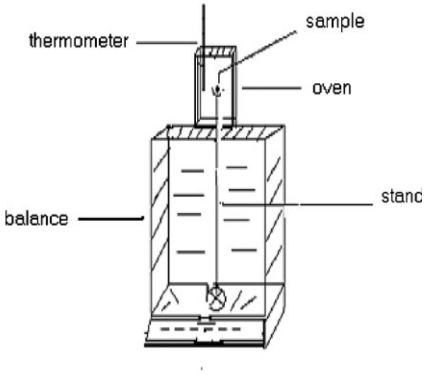

Figure 1.
Apparatus used in monitoring the weight of samples.

Mixing of Phenolic wax with HDPE

The Ph-Wax antioxidant was mixed with HDPE in the ranges (0.2, 0.4, 0.6 and 0.8) % wt/wt the two components mixed well for 15 min.

Oxygen Uptake Measurements

0.1 g of the sample was placed in the sample tube of oxygen uptake apparatus, then it was filled with O_2 gas, the temperature was raised to 230 °C; then the pressure of the tube was adjusted with atmospheric pressure.The oxidation measurements were carried out by monitoring the O_2 absorption by the sample volumetrically.

Thermal Stability Measurements

The thermal stability of these samples was evaluated isothermally at 250 °C, and under air atmosphere by monitoring the changes in the weight of the samples due to the effect of heat and air (O_2).

Results and Discussion

Figure 2 and 3 show the infrared spectra of the Cl- wax and the grafted Ph – Wax, respectively; the spectrum of Cl – wax, Figure 2, shows the bands at (600–800) cm^{-1} and at 1450 cm^{-1} which correspond to the peaks of (C–Cl) bonds and to ($-CCl_2$) groups. The infrared spectrum of grafted ph-wax, Figure 3, shows a characteristic peak at 3450 cm^{-1} for asymmetrical stretching of free hydroxyl groups of phenol, with another peak at 1630 cm^{-1} for the double bonds in benzene rings. Moreover, the peak of C–Cl bond that appeared at (600–800) cm^{-1} in Cl-wax

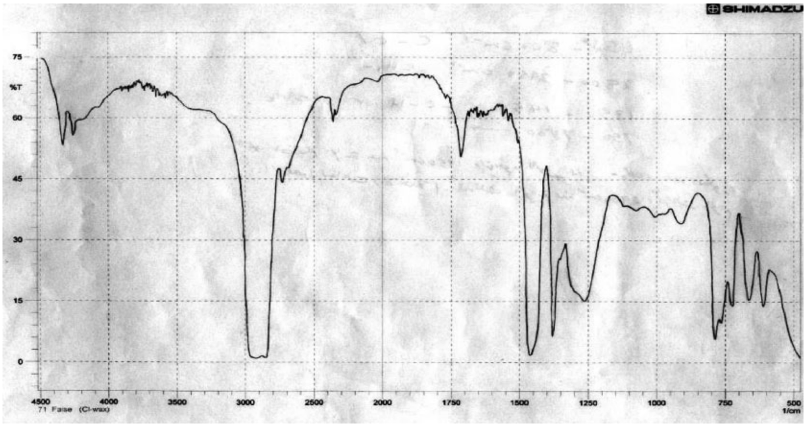

Figure 2.
FTIR of Cl-wax.

decreased after the substitution of wax with phenolic groups. HDPE undergos oxidation reaction by atmospheric O_2, and the oxidation rate depends on some factors, such as heat and light that can accelerate oxidation reactions. However, Figure 4 shows the oxidation of HDPE polymer free of additive and with ph - wax at deferent percents; at 230 °C and under O_2 atmosphere. From Figure 4, its clear that the resistance of polyethylene to oxidation increases with increasing the percentage of

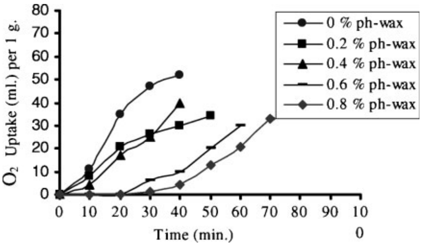

Figure 4.
O_2 uptake by HDPE in the presence of ph-wax at 230 °C

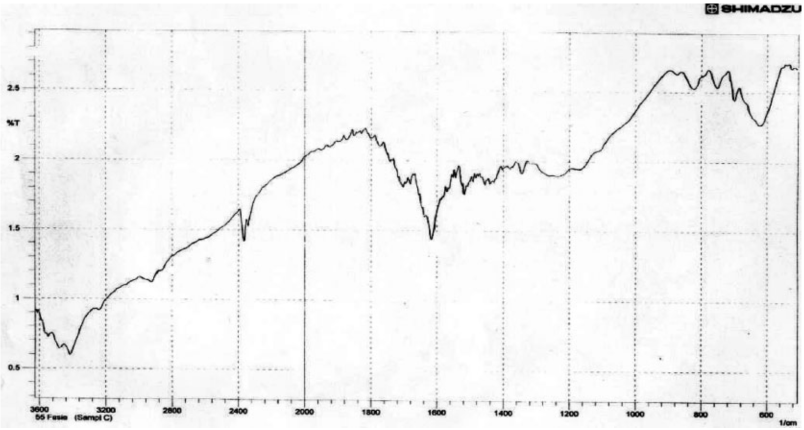

Figure 3.
FTIR of ph -wax.

the ph – wax, this effect is results from the performance and action of phenolic groups on phenolic polyethylene wax, whereas these groups can act as proton donors for free radicals that occur in polymer during oxidation process[4,11,12]. From Figure 4, the curves of oxidation of pure HDPE started at (4–5) min. from heating and also the oxidation rate was about (2) ml O_2/min. although the oxidation reactions continuoued for more than (40)min., while the oxidation reactions started at (5–8)min. when phenolic wax percent was (0.2) % at oxidation rate 0.96 ml O_2/min.and this time increased to reach about (25–30) min., (0.6) ml O_2/min. and (35–40)min., (0.5) ml O_2/min. for the percent of phenolic wax is (0.6) % and (0.8) % respectively. In general, the oxidation reaction rate of all the samples decreased with the increase of percent of additive; the possible explanation for this behavior is that, the phenolic wax acts as an active antioxidant. There are some positive factors that play a key role for this affection, one of them is the hydrocarbon chains of wax which give stearically hindrance for phenolic groups, and raise the compability between this derivate and polyethylene. On the other hand, the thermal stability of HDPE in the presence of phenolic wax was studied by monitoring the weight loss of the samples. Figure 5, shows the thermograms of pure HDPE and with deferent percents of the ph-wax, in which there is a significant increase in the weight of pure HDPE which started after (1) min. with rate of about (0.16) %wt/min. It is well known that this increase in the weight of the sample was due to the reaction with O_2; in fact this polymer undergos extensive oxidation, moreover, the oxidation process continued for (80) min., then a decrease in weight appeared after (160) min. This indicates that the polymer continued to oxidize for (80)min. and then started to decompose and lose CO_2 and H_2O, etc. Moreover, the thermograms of these samples, Figure 5, show a decrease in the amount of O_2 that reacted with polyethylene containing Ph-Wax, also the decrease in the rate of thermograms was (0.16) %wt/min. for pure HDPE, while (0.14) %wt./min. and (0.03) %wt./min. for (0.4) % and (0.6) % samples, respectively, while at (0.8) % sample, there was no increase in the weight of the sample during heating it for (20)min. Then a decrease in weight appeared as a result of decomposition, this effect may be due to the action of phenolic wax as an antioxidant by claim-breaking mechanism by donor proton to active free radicals into polymer chains. Many phenolic commercial antioxidants have low molecular weight therefore can be lost from polymers by evaporation and/or extraction,[13] but the grafted phenolic wax has high molecular weight which minimizes the decrease in its concentration from the polymer during long-term uses. Phenolic wax has this advantage, accordingly, this derivative continues to act as an antioxidant for a long time. Figure 6 shows the thermal stability of phenolic wax; there is no significant degradation stage during heating at 250 °C for more than

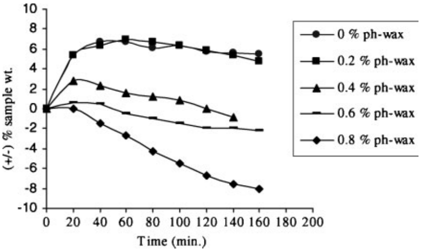

Figure 5.

Thermograms of HDPE pure and with ph - wax at 250 °C and under air atmosphere.

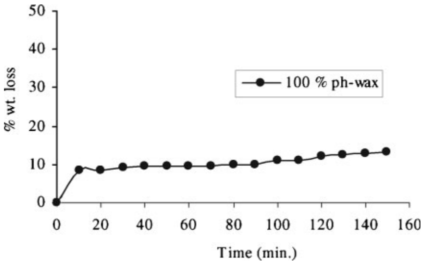

Figure 6.

Thermograms of phenolic wax at 250 °C and under air atmosphere.

(100)min. except for the little weight loss which occurred after (1–5) min., this may be attributed to the moisture in the sample.

Conclusion

The preset study shows significant improvement in resistance of HDPE to thermal oxidation-degradation process by O_2 and heat by using phenolic polyethylene wax. The compability and low volatility of this derivative led to further activity in it's action as antioxidant, the data of the monitoring of the O_2 uptake and the changes in the weight of the samples, show the higher performance for this additive when used at (0.6) % and (0.8) % per weight of polymer. Therefore, using this product at this percent was practically for commercial uses and applications.

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