



Characterization of Polyethylene Carrying Bags Before and After Isothermal Oxidative Aging in an Oven

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Abstract: Utility of polymeric material is a major contribution to the production of waste, particularly in Pakistan. An easy escape to it is the dumping in the land which is not commendable for an environmental point of view. On the other hand, the aging of polymer is analogous to its burial conditions under the soil in the absence of light. Therefore, in this research report, two different brands of polyethylene carrying bags were investigated. One sample was obtained from Pakistan abbreviated as sample "Y" while the other from Canada abbreviated as "E". In order to accelerate the degradation process and to observe the impact of aging in a shorter span of time, these samples were heated at an elevated temperature (80°C) in an oven for the period of 20 days. The samples were characterized before and after aging with an interval of 2 days by applying different techniques like FT-IR, SEM, DSC, and thermogravimetric analysis (TGA). Carbonyl peak at 1715 cm⁻¹ was observed only in the case of sample "E" displaying carbonyl index value as 28.45 % after 20 days of aging. The SEM images before and after aging revealed that the degradation took place at preferential sites in case of sample "Y" and at numerous sites in case of sample "E". The results of percent crystallinity obtained by DSC showed an increasing pattern with aging for both the samples and was high in case of sample "E." The activation energy determined by using Flynn-Wall-Ozawa showed a decreasing pattern for both the samples with aging. It concluded that the thermal aging initiates the process of degradation which was then accelerated by heating in TGA oven. The order of reaction was slightly decreased after aging for both the samples and was found to be independent of the heating rate.

Keywords: Carbonyl Index, Percent Crystallinity, Oxidative Induction Time, Scanning Electron Microscopy, Thermogravimetric Analysis.

1. Introduction

The worldwide production of polymeric material is increasing with the passage of time due to its versatile properties and reached up to 322 Metric tons in 2015 [1]. On the other hand, their waste management has become one of the most concern issues-particularly in developing countries like Pakistan due to the long life of such material, population boom, and not having proper management and recycling facilities. Moreover, scientific development has provided several facilities to human beings for their ease, which may ultimately give birth to several issues like polymeric packing material and shopping bags. As such material has quite a long life and is not biodegradable, hence a noticeable amount of plastic waste is accumulated in the cities with time. Among this polyethylene is one of the most commonly used polymers (about 60%) in modern society [2]. Unfortunately, its recycling is neither always easy nor profitable, hence a significant quantity of its waste is dumped inland and in streets [3]. The literature reveals that about 65% of waste is land-filled, 25% is reused and 10% is

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recycled both chemically and mechanically [4]. This solid waste, which is even more than 65% in developing countries, is generating robust health and environmental impacts. Therefore, the scientists are trying hard to explore various ways and means to make use of this waste by recycling it, which is considered to be much beneficial method among all as one can get the product which can be useful. These can either be gas, liquid or solid or some petroleum products. However, to design a technology the information regarding the mechanism, thermodynamics and kinetics of the process are required [5]. The scientists are working over it by investigating the aging/degradation process under various conditions like aging under accelerated conditions [6, 7], the impact of water over aging etc. [8]. However, increasing the number of parameters complicates the mechanism of degradation and becomes difficult to understand and conclude. Therefore, we have planned to thermally degrade the polyethylene shopping bags samples under air by heating the samples in the oven and characterized them by using various latest techniques. The kinetics of degradation before and after thermal aging was investigated by using thermogravimetric analysis.

Theoretical background

Generally, the decomposition reaction of the polymeric materials can be expressed as:



Here, the symbols A, B, and C, represent the "initial", "residue" and "gaseous" materials, respectively. The data obtained from the thermogravimetric analysis can be utilized for the kinetic study and the "degree of conversion, α ". The degree of conversion is defined as:

$$\alpha = \frac{W_0 - W_t}{W_0 - W_\infty} = \frac{\Delta W}{\Delta W_0} \quad (2)$$

Where " α " is "degree of conversion", " W_0 " is "initial weight", " W_t " is the "weight of sample available at time t" and " W_∞ " represents the "final weight of the sample".

The kinetic process may be expressed by a typical model:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (3)$$

Where, " $d\alpha/dt$ ", " k ", and " $f(\alpha)$ " denote the "decomposition rate", "decomposition rate constant" and the "differential expression", respectively for a "kinetic model function".

The dependency of " k " on the temperature can be represented by "Arrhenius expression"

$$k = A \exp \left[\frac{-E_a}{RT} \right] \quad (4)$$

Here, " A " is the "pre-exponential factor (1/sec)", " E_a " is the "activation energy (kJ/mol)", " R " is the "general gas constant (8.314 J.mol⁻¹. K⁻¹)" and " T " is the "absolute temperature (Kelvin)".

Combining equations (3 and 4) gives

$$\frac{d\alpha}{dT} = A \exp \left[\frac{-E_a}{RT} \right] f(\alpha) \quad (5)$$

Considering the variation in temperature is " β " ($=dT/dt$), a steady heating rate then we get:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp \left[\frac{-E_a}{RT} \right] f(\alpha) \quad (6)$$



Therefore, equation (6) is the very basic equation for the investigation of the kinetics of degradation of material by using the results one gets from the thermogravimetric analysis [9]. A number of methods have been presented for the determination of the energy of activation of thermal degradation of polymers, however, we applied the Flynn-Wall-Ozawa method which is a well-accepted method for the purpose and is an integral one [10-12]. The Flynn-Wall-Ozawa method is also entitled as a model-free method as it is based on the hypothesis that the rate of thermal degradation reaction depends on the temperature only for a particular degree of conversion and hence, it is considered as the most authentic method in this regard [13]. The activation energy "E_a" can be determined by using the Flynn-Wall-Ozawa method without bothering about "order of reaction". It can be expressed in terms of equation (7)

$$\log \beta = \log \frac{AE_a}{g(\alpha)R} - 2.315 - \frac{0.4567E_a}{RT} \quad (7)$$

Where "A" and "R" are constants for a particular conversion, "g (α)". The activation energy (E_a) can be determined from the slope of the curve obtained from the plots of "log β" vs "1/T" at different heating rates for any particular "degree of conversion" (α).

Determination of order of reaction

The "order of reaction," "n" and the "pre-exponential factor" "A" was obtained using equation (8) [9]

$$\ln \left[\frac{\beta d\alpha/dT}{\exp(-E_a/RT)} \right] = \ln A + n \ln(1 - \alpha) \quad (8)$$

The "n" and "A" was obtained by plotting $\ln \left[\frac{\beta d\alpha/dT}{\exp(-E_a/RT)} \right]$ versus $\ln(1-\alpha)$ in which slope gave the value of "n" and intercept was equal to $\ln A$.

2. Materials and methods

Materials

Two samples of polyethylene carrying bags of different brands were analyzed. Sample "Y" was made in Pakistan, which was widely used for grocery/carrying purposes. It was purchased from the local market sold under the brand name of "Special Yaadgar." It was having a light green color and was in the form of a film having a size of 25.40 x 33.02 cm. Its thickness was measured which was 0.01 mm. This sample was named as sample "Y" and "Yd" after oven aging. Here d stands for no of days for which it was aged in the oven. Sample "E" was supplied by "Econogreen Plastics," Canada. According to the producer, the sample was made from 100 % recycled plastic and was 100 % recyclable material and will be itself completely degraded in 2 years. It was further claimed that these bags were oxo-degradable and contained a unique agent that helps in breaking down carbon-carbon bonds in the material and reduces its strength when exposed to oxygen. These polyethylene bags were in the form of a film having black color, and its capacity was 127 L. Its thickness was 0.03 mm which was slightly greater than that of sample "Y". According to the requirement of analysis, this sample was abbreviated as "E" and "Ed" before and after aging (d= no of days) in the oven, respectively. The exact composition of both of these polyethylene samples was not disclosed by the suppliers, being a business secret and were used as received.



Methods

Oven aging

The polyethylene films of sample "Y" and "E" were cut into fine strips of dimensions 38x13 mm with the help of a blade. These strips were placed in Petri dishes without any lid and were kept in an electric oven in the air atmosphere. The Electric Oven used for the purpose was 5890A GC, Hewlett Packard, made in the USA. The temperature of the oven was raised at the heating rate of 20 °C/min from ambient to 80 °C and was kept constant for 20 days. The samples were subjected to characterization using various techniques after 20 days of oven aging with an interval of 2 days.

FT Infrared spectroscopic measurements

Tensor 27, FT-IR spectrophotometer supplied by Bruker, Germany, was used to measure the IR spectra of the samples. The interpretation of the spectra was made by using the software OPUS Version 4.2 Build.

Carbonyl index measurement

For this purpose, the same IR instrument was used. IR is considered to be very susceptible to chemical changes that may have taken place during the exposure to thermal aging [14]. The rate of formation of carbonyl groups of the samples during thermal treatment was calculated in terms of carbonyl index (CI), which gave a numerical value and estimation of the degree of oxidation for each polyethylene sample [15]. For the calculation of the carbonyl index, the area of the peak at 1715 cm⁻¹ and a reference peak at 2923 cm⁻¹ was considered using equation (9) [16, 17].

$$\text{Carbonyl index} = \frac{(\text{Area of absorbance at } 1715 \text{ cm}^{-1})}{(\text{Area of absorbance at } 2923 \text{ cm}^{-1})} \times 100 \quad (9)$$

Scanning electron microscopic measurement

For the investigation of the morphology of the samples, Carl Zeiss LEO 1530 scanning electron microscope, made in Germany, was used. The Gemini field emission columns (FESEM) and EDX/OIM PV9715/69 ME were also coupled with this microscope. The sample films after aging were dried and sputtered with a gold coating having a thickness of approximately 10 nm. During this procedure, Argon was used, being an inert gas. These sample films were fixed on an aluminum stub with the help of double-sided conductive tape.

Measurement of oxidative induction time

The OIT (oxidative induction time) was measured by using Differential Scanning Calorimeter, DSC Q2000 manufactured by TA Instruments, made in Canada. Throughout the procedure, ASTM No D-3895-07 was strictly followed. For the interpretation of data "Universal Analysis 2000 (TA Instruments, Version 4.5A Build 4.5.0.5)" software was used provided with the instrument. For this analysis, first of all, the sample films were converted into sheet formats (thickness of 200 ±15µm) by using conversion-molding. In order to get a required sample size, these sheets were cut into specimen disks with the help of a punch machine having a diameter of approximately 6.4 mm. The specimen disk of sample Y was placed in the DSC's sample container compartment without covering with the lid. The samples were heated with a heating rate of 20°C/min from 30 to 200°C (set-point temperature) under a nitrogen atmosphere with a constant flow rate of 50 mL/min. The heating was discontinued at the set-point temperature and the sample was allowed to equilibrate at this temperature for 5 min. After 5 min, the ambient atmosphere was shifted from nitrogen gas to oxygen gas with the same flow rate. The change-over point to oxygen gas was termed as zero time and isothermal heating (200 °C) was continued until an exotherm was observed.



Percent crystallinity measurement

The percent crystallinity of both the samples was determined before and after aging by using the same "DSC Q2000". The samples were heated at from 30 to 200 °C heating rate of 10 °C/min and were kept as an isothermal mode for five minutes and then cooled at the same rate from 200 to 30 °C. During this investigation, nitrogen gas was used as being inert in nature at a constant flow rate of 50 ml/min. The percent crystallinity was determined from the DSC curves by using the following relation:

$$\text{Percent Crystallinity} = \left[\frac{\Delta H}{\Delta H_0} \right] \times 100 \quad (10)$$

Here " ΔH " is the enthalpy of fusion of the sample obtained from DSC results. The " ΔH_0 " was the enthalpy of fusion of polyethylene in 100 percent crystalline state and taken as equivalent to 290 J/g for polyethylene samples [18-20].

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out by using a Q500 TGA instrument supplied by TA Instruments, Canada. The samples were placed in the furnace using platinum pans of the TGA instrument, and nitrogen gas were pumped at a constant flow rate (50 ml/min) to have inert atmosphere and heated at various heating rates (5, 10, 15, and 20°C/min). The activation energy (E_a) of thermal degradation of the samples was obtained by employing the Flynn-Wall-Ozawa method [10-13] while the order of reaction "n" and the pre-exponential factor "A" was calculated by applying equation (8) [9].

3. Results and discussions

FT Infrared spectroscopic analysis

The IR spectra of sample "Y" before and "Y20" after aging in the oven for 20 days almost overlapped upon each other (Figure 1). The major characteristic peaks of polyethylene were observed at 2920, 2850, 1463 and 720 cm^{-1} , which were assigned to -C-H asymmetric stretching, symmetric stretching, -C-H bending, and -C-C rocking, respectively. Another small peak was observed for both the samples at 2369 cm^{-1} which might be due to the absorption of CO_2 in this region. It has been reported that the FTIR spectra (from 1400 to 1300 cm^{-1}) can be exploited to differentiate the polymer sample from low to high-density polyethylene [21]. This technique was applied to both the samples before aging concluding that the sample "Y" was "HDPE" and sample "E" was "LLDPE". The IR spectra of sample "Y20" concluded that the aging process had no effect in this region (1400 to 1300 cm^{-1}); whereas the previous study revealed that it was changed from HDPE to LLDPE if it was exposed to accelerated weathering conditions in which UV radiations and humidity/ water contents were additional constraints [6].

The IR spectra of sample "E" and "E20" are depicted in Figure 2 showing the same characteristics peaks of polyethylene and CO_2 along with the emergence of two new peaks at 1170 and at 1715 cm^{-1} . The C-O-C stretching was observed at 1170 cm^{-1} and formation of carbonyl groups during the aging process as indicated by the peak observed at 1715 cm^{-1} . The sample films were analyzed by FT-IR after aging with an interval of 2 days and no carbonyl peak was observed even up to 12 days of aging. However, after 14 days a small carbonyl peak was observed whose intensity was gradually increased with the aging time. While after 20 days, its intensity was significantly enhanced. The carbonyl index was calculated by using equation (9). The value of the carbonyl index for sample "E" came out as 28.45 % which was quite significant. The formation of carbonyl species during the aging of polymer samples concluded the oxidation of polymer during processes. It has been reported that aldehyde and ketone carbonyl groups are commonly formed during the thermal aging process which is significantly important for further degradation of polymers [22]. Further, the IR spectra of sample "E20" was magnified in the range of 1400 to 1300 cm^{-1} and it was concluded that the "E20" sample was "LLDPE"

as no changes were observed after aging. Keeping in view the carbonyl index and IR spectra of both the samples before and after aging, it was concluded that the aging process introduced some chemical modification in the sample "E" and the formation of oxygenated products was formed. This observation was in accord with the literature and that the oxidation rate of LLDPE was slightly higher than that of HDPE, despite the thickness of the samples film which may limit oxygen diffusion [23-25].

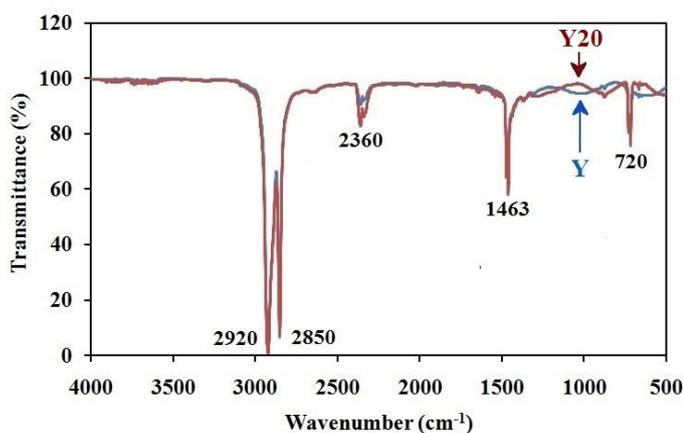


Figure 1. IR spectra of sample "Y" (before) and "Ya20" (after aging for 20 days in an oven).

It was further presumed that the additives in the sample "E" were more susceptible to thermo-oxidative degradation while in the case of sample "Y" these were thermo-stabilizer in nature as sometimes shelf life is more important than anything else [26]. It is well recognized that if metals are added to polyolefin then the polymers can be easily thermally oxidized. For example, Manganese (Mn) is a suitable metal for pro-oxidant activity. Further to it, on thermal treatment of polymers in the presence of oxygen free radicals are produced which can further oxidize the polymer. Such a phenomenon results in variation in physical and mechanical properties[27]. It is also expected that this phenomenon may result in the formation of -COOH, -OH, C=O groups [28].

Scanning electron microscopic Analysis

The film of both the samples was taken out from the oven after an interval of 2 days and analyzed by scanning electron microscopy. The SEM micrographs did not show any detectable change in the morphology up to 12 days of aging for sample "Y". However, after 14 days of aging the wrinkles and etching process were noted (Figure 3a). The SEM images of sample "Y20" aged for 20 days indicated that the wrinkles became deep and converted to cracks, and ultimately the film was torn up at some specific sites (Figure 3b).

Similar morphological changes were observed in the sample "E14", aged for 14 days in the form of small cracks (Figure 4a). The SEM images of sample "Ea18", aged for 18 days demonstrated the initiation of degradation process (Figure 4b). Figure 4b displayed that the film was swollen up in the form of big flakes. It may be due to the bursting of additives because of prolonged exposure to heat and oxygen. The SEM image of sample "E20", aged for 20 days highlighted the formation of grooves, pitch, cracks, and flakes at numerous sites, which ultimately lead to the tearing up of the film (Figure 4c).

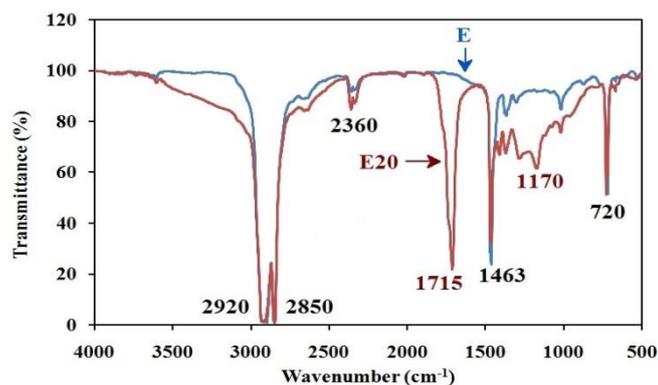


Figure 2. IR spectra of sample "E" (before) and "Ea20" (after aging for 20 days in an oven). The emergence of carbonyl peak at 1715 cm^{-1} can be observed.

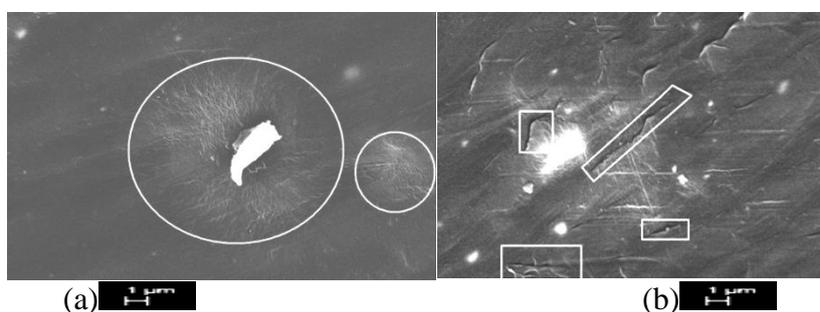


Figure 3. SEM image of sample "Y" after aging in an oven under air atmosphere for (a) 14 days (b) 20 days. Encircled portion indicates the etching and the formation of wrinkles in the film and formation of cracks resulting in tearing of the film.

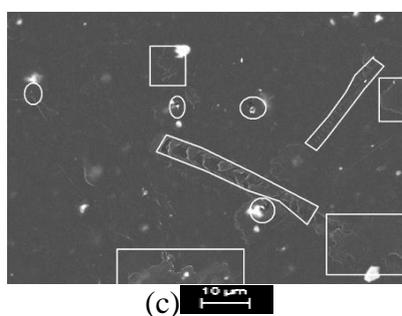
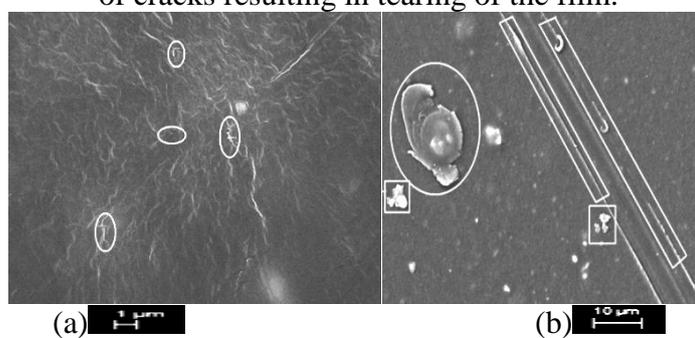


Figure 4. SEM image of sample "E" after aging in an oven for (a) 14 days (b) 18 days and (c) 20 days. Enclosed portion indicates the initiation of the cracking process in the film.

SEM images concluded that the aging in the oven had less effect on sample "Y" as compared to sample "E". In case of sample "E", the oven aging showed a drastic effect by instigating the breaking of the film at numerous sites. The main factors influencing the process of degradation were the presence of pro-oxidant [23]. These observations were also supported by the results obtained through IR analysis.

Oxidative induction time

The oxidative induction time (OIT) of the material under investigation was measured prior to aging with the help of the DSC instrument. The oxidative induction time was 41 minutes and 5 minutes for sample "Y" and "E," respectively, concluding that sample "Y" was thermally more stable and contained a higher amount of antioxidants as compared to sample "E" [29].

Percent crystallinity measurement

Both the samples were analyzed before and after aging for percent crystallinity by using DSC. The 1st cycle of the temperature scan was considered as it enclosed the thermal history of the sample [30]. The percent crystallinity of both the samples determined by applying equation (10). The values obtained prior to aging was 49 % and 31 % for sample "Y" and "E", respectively. For the investigation of the impact of aging over percent crystallinity of the samples, the samples were taken out from the oven after an interval of two days and were analyzed by DSC and percent crystallinity was determined. It was noted that there was no significant change in the value up to 12 days of aging and was slowly increased after 14 days of aging and obtained the value 52 % and 43 % for sample "Y20" and "E20", respectively after 20 days of aging. The DSC curve of the sample "Y20" is shown in Figure 5.

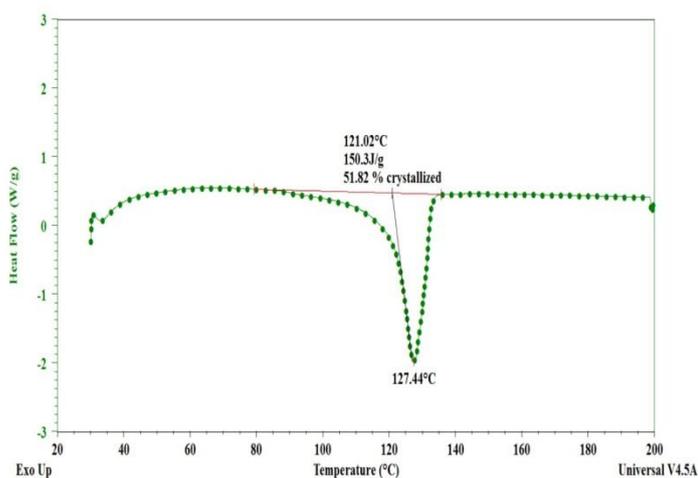
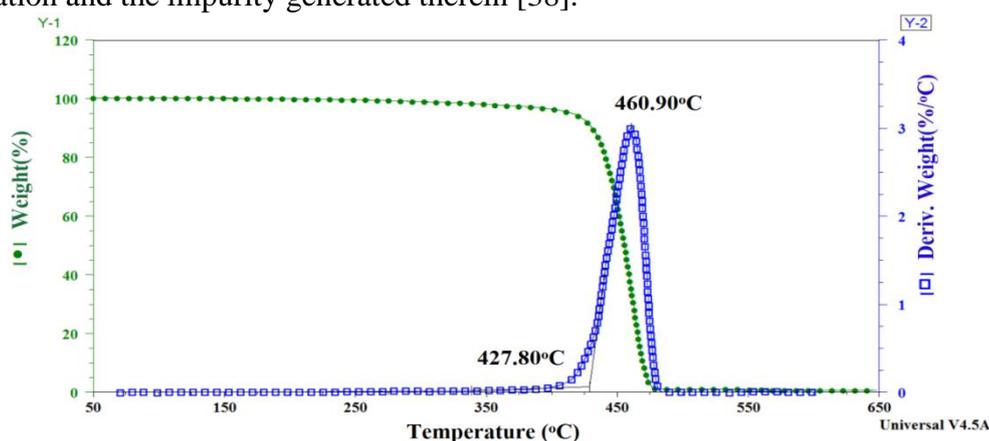


Figure 5. Percent crystallinity of the sample "Y20" determined by using DSC.

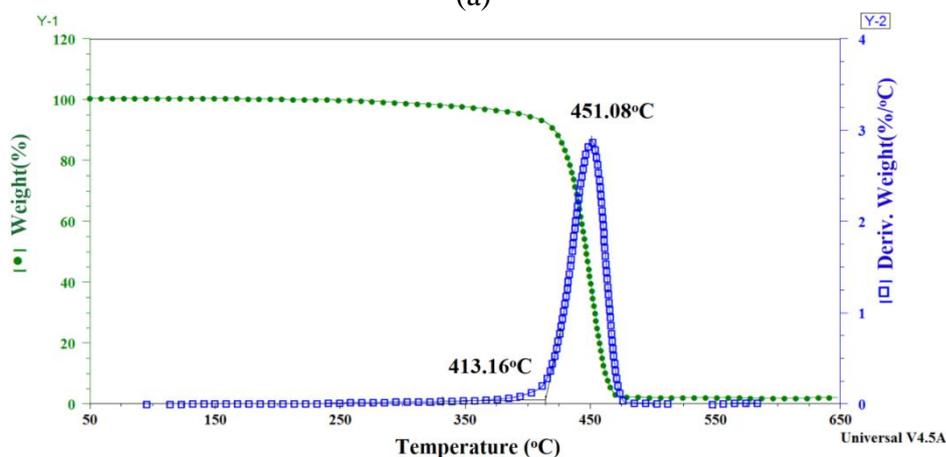
However, it was 63 % for sample "Y" and 47 % for sample "E" on their exposure to UV light, humidity and high temperature simultaneously, using the QUV chamber for 20 days [6]. It was concluded that these parameters had a significant impact as compared to oven aging. The increase in percent crystallinity was higher for sample "E" as compared to sample "Y". The reason behind the increase in the value of percent crystallinity may be attributed to the chain scission and also because of the combination of small entangled molecular fragments due to which the re-crystallization process may have taken place [31-34]. The melting point of sample "E" was decreased from 122.14 °C to 119.95 °C and that of sample "Y" remained constant at 127.02 °C after the aging of 20 days. The results of OIT, C.I, and SEM images concluded that the additives in the sample "E" were more vulnerable to thermo-oxidative degradation.

Thermogravimetric analysis

The thermogram of the sample "Y" before and after aging for 20 days was recorded at various (5, 10, 15 and 20 °C/min) heating rates showed a single DTG peak, indicating that the degradation was a single step process irrespective of aging (Figure 6 (a = before aging, b = after aging of 20 days)). The onset temperature " T_o " for 5 °C/min heating was 427.80 °C prior to aging and 413.16 °C after 20 days of aging. The same decreasing trend was observed (460.90 to 413.57 °C) for the high heating rate (20 °C/min). As " T_o " is considered to be an indicator of thermal stability so a decrease in " T_o " with aging concluded a decrease in thermal stability of these samples due to prolonged heating and particularly in the air atmosphere [35]. The thermogram of sample "E20" obtained at these four heating rates displayed also single DTG peak indicating a single step degradation mechanism as it was observed prior to aging. For instance, the thermogravimetric curves of sample "E" at a heating rate of 5 °C/min are depicted in Figure 7 (a = before aging, b = after aging of 20 days). The onset temperature " T_o " calculated at 5 °C/min heating rate was decreased from 414.58 °C to 402.86 °C due to aging. Similarly, the peak temperature " T_p " was also decreased from 465.38 to 457.81 °C at the same heating rate due to aging. The broadening of DTG peak, lowering of " T_o " and " T_p " can be due to aging, which may have converted high molecular weight polymer material into smaller molecular fragments as these parameters are the molecular weight of polymer dependent [36]. Heating above 200 °C may lead to chain scission, and the nature of the product may be dependent on the impurities, presence of unsaturated sites and head-to-head units, etc.[37]. Further, the Poly-olefins may be susceptible to thermal oxidation and the impurity generated therein [38].

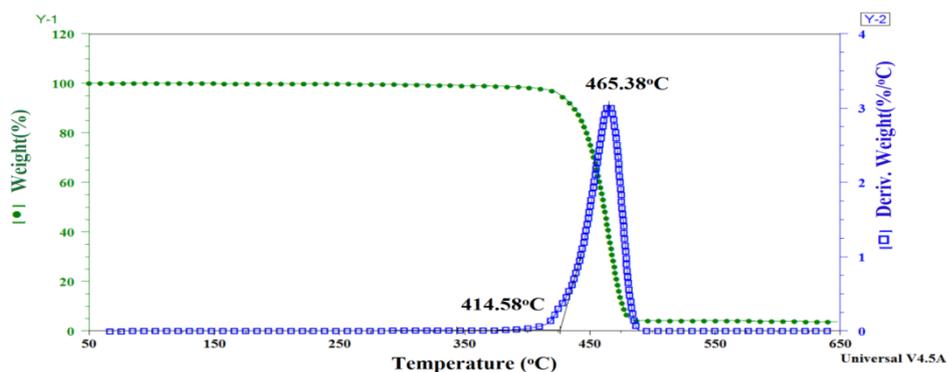


(a)

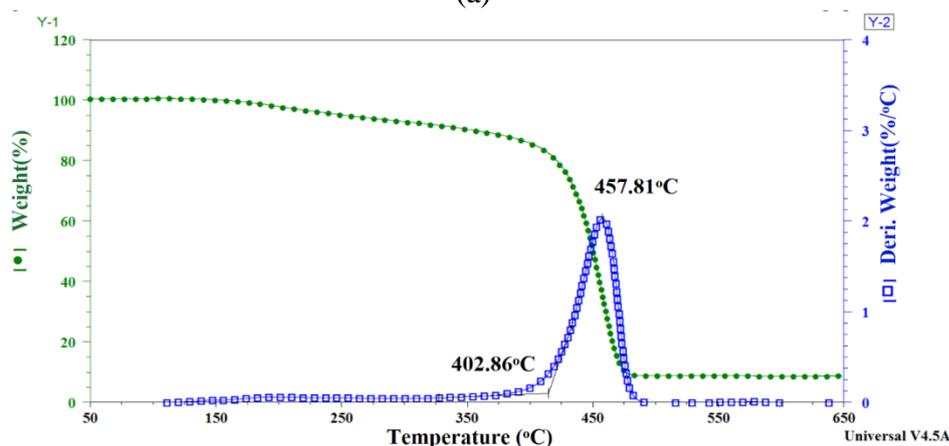


(b)

Figure 6. Thermograms of sample "Y" at a heating rate of 5 °C/min (a) Before and (b) After aging in an oven



(a)



(b)

Figure 7. Thermograms of sample "E" at a heating rate of 5°C/min (a) Before and (b) After aging in an oven

Keeping in view these results, it has been concluded that the thermal degradation mechanism of polyethylene under the nitrogen atmosphere before and after aging in an oven proceeded through a single step degradation. It has also been observed that the thickness of the film has a significant impact on the degradation during the thermogravimetric analysis as perceived by others [35]. It was reported that the high heating rate (20 °C/min) has little effect over the shifting of onset temperature that may be due to lagging behind the sample temperature as compared to the furnace temperature [39]. It has been further concluded that the onset temperature (T_0) played a key role in accessing the stability against the heat and aging phenomenon of the materials and that the aging has a pronounced effect on sample "E" as compared to sample "Y".

The activation energy of thermal degradation

The thermograms obtained at 5, 10, 15 & 20 °C/min heating rate under the atmosphere of nitrogen before and after aging of samples "Y" and "E" were utilized and activation energy (E_a) of thermal degradation was obtained by applying the Flynn-Wall-Ozawa method [10-13]. It is among the basic methods employed for the calculation of " E_a " without the knowledge of the order of the reaction. The " E_a " was obtained from $d(\log \beta)/d(1/T)$ obtained by plotting " $\log \beta$ " versus " $1/T$ " (T = The corresponding temperature of each specific degree of conversion) (equation 7) for different heating rates (β) for any particular degree of conversion (α).



Table 1. Activation energy (E_a) of samples "Y" and "E" determined by Flynn-Wall-Ozawa method before and after aging in an oven

Degree of conversion (α)	E_a (kJ/mol)			
	Sample "Y"		Sample "E"	
	Before aging	After aging	Before aging	After aging
0.1	158	65	357	81
0.2	165	87	649	104
0.3	171	180	549	123
0.4	174	186	472	238
0.5	180	177	419	357
0.6	184	177	382	368
0.7	189	170	351	290
0.8	192	169	327	225
0.9	198	166	307	185
Mean " E_a " (kJ/mol)	179	153	424	219

The " E_a " obtained in this way for sample "Y" and "E" before and after aging (TGA performed under nitrogen) is displayed in Table 1. The " E_a " of sample "Y" before aging was 158 (kJ/mol) at $\alpha = 0.1$ and was gradually increased up to 198 (kJ/mol) with the increase in the degree of conversion up to $\alpha = 0.9$. The mean value of " E_a " was obtained as 179 (kJ/mol) as reported in the literature [6]. It is also reported in the literature, that the value of " E_a " for polyethylene gradually increases from 150 to 240 (kJ/mol) with the increase in the value of the degree of conversion (α) [40].

It was noted that after aging, the " E_a " was very low at $\alpha = 0.1$ (65 kJ/mol) and increased up to 186 (kJ/mol) at $\alpha = 0.4$. The " E_a " became almost constant (177 kJ/mol) at $\alpha = 0.5$ to 0.6 and then showed a decreasing trend from $\alpha = 0.7$ to 0.9. The mean value of " E_a " was equal to 153 (kJ/mol) which was less than prior aging it may be due to change in the mechanism of degradation due to heating for longer and at high temperature [35].

The " E_a " of sample "E" before aging was 357 (kJ/mol) at $\alpha = 0.1$ and was abruptly increased to 649 (kJ/mol) at $\alpha = 0.2$. It was then decreased from 549 to 397 (kJ/mol) when α was varied from 0.3 to 0.9. It was observed that the mean values of " E_a " for sample "E" was relatively high (424 kJ/mol) [6]. The " E_a " of sample "E" after aging was very low (81 kJ/mol) at $\alpha = 0.1$ and was increased with the increase in the degree of conversion and attained the value up to 368 (kJ/mol) at $\alpha = 0.6$ and then decreased with the increase in α . The mean " E_a " was equal to 219 (kJ/mol) which was about 50 % less than the " E_a " determined prior to aging (424 kJ/mol). However, it was greater than the mean " E_a " of sample "Y20" and has been well established that the thickness of the film of the material may influence over the TGA results and films of sample "E" were thicker than the film of sample "Y" [35].

Order of reaction

The order of reaction (n) and pre-exponential factor (A) for these samples were determined before and after aging by using equation (8) from the TGA curves obtained at a heating rate of 5, 10, 15, and 20 °C/min.

Table 2. "Order of reaction" and "pre-exponential factor" obtained from TGA curves for sample "Y" before and after aging in an oven

β °C/min	Before aging			After aging		
	n	$A(10^{26}/s)$	R^2	n	$A(10^{10}/s)$	R^2
5	1.06	7.0	0.990	0.99	4.9	0.981
10	0.97	6.9	0.997	1.04	4.7	0.967
15	0.99	4.6	0.997	1.01	4.6	0.981
20	0.98	3.6	0.995	0.88	5.1	0.994
Mean	1.00	5.5	-----	0.98	4.8	-----
Standard deviation	± 0.04	± 1.7	-----	± 0.07	± 0.22	-----



Table 3. “Order of reaction” and “pre-exponential factor” obtained from TGA curves for sample "E" before and after aging in an oven.

β °C/min	Before aging			After aging		
	n	A(10^{18} /s)	R ²	n	A(10^7 /s)	R ²
5	0.73	2.8	0.927	0.87	4.7	0.901
10	0.96	3.7	0.990	0.73	4.6	0.919
15	1.05	4.7	0.988	0.93	3.1	0.971
20	1.05	4.8	0.991	0.95	4.5	0.992
Mean	0.95	4.0	-----	0.87	4.2	-----
Standard deviation	± 0.15	± 0.94	-----	± 0.10	± 0.75	-----

It can be seen from table 2 and 3 that the order remains the same with the increase in heating rate from 15 to 20 °C/min. However, a slight change in its value was observed as we move from low to high heating rates. The mean value of the order of reaction for sample "Y" was 1.0 (± 0.04) and after aging, it was slightly decreased to 0.98 (± 0.07). The value of the pre-exponential factor was drastically decreased from 5.5×10^{26} /s (± 1.7) to 4.8×10^{10} /s (± 0.22) with aging. The order of reaction of sample "E" was 0.95 (± 0.15) and was decreased to 0.87 (± 0.10) with aging. The value of the pre-exponential factor was also decreased with aging from 4×10^{18} /s (± 0.94) to 4.22×10^7 /s (± 0.75).

The results concluded that the order of reaction was almost independent of the heating rate as the degradation of polyethylene occurs through random chain scission [41]. The impact of aging was visible from the results of FT-IR spectroscopy, SEM, and DSC techniques.

4. Conclusions

Two samples of polyethylene carrying bags; one was made in Pakistan, symbolized as "Y" while the other was from Canada, symbolized as "E" were analyzed with reference to the impact of thermal aging in an oven. The interpretation of the IR spectra revealed that the sample "Y" was "HDPE" while the sample "E" was "LLDPE." IR spectroscopy also indicated the formation of carbonyl peak at 1715 cm^{-1} only in case of sample "E" during aging and its intensity was increased with the increase in aging time and attained the value of 28.45 % after the period of 20 days. The emergence of carbonyl peak manifests that the oxidative degradation has taken place in which the main contributors were the additives in sample "E" that were pro-oxidant in nature. The higher value of OIT for sample "Y" as compared to sample "E" concluded that the additives in sample "Y" were anti-oxidant in nature. It was confirmed from the SEM images that the oxidative degradation took place at preferential sites in case of sample "Y" while at numerous sites in sample "E". Aging processes encouraged the re-crystallization process as the percent crystallinity of both the samples was increased during aging. The apparent activation energy and pre-exponential factor of both the samples were decreased after aging. A slight decrease in the value of the order of reaction was observed and it was concluded that the value of the order of the reaction is independent of heating rate. Further to it, the results obtained by all the techniques were consistent and supported each other. It is interesting to note that all these samples of polyethylene showed a similar trend and hence it can be concluded that the nature and concentration of the additives played a crucial role in controlling the degradation mechanism of the polymeric materials.

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Abbreviations

A = Pre-exponential factor, s^{-1}

CI = Carbonyl Index

DSC = Differential Scanning Calorimetry

DTG = Derivative Thermogravimetry

E = Sample Econogreen Plastic

Ea = Activation Energy, kJ mol^{-1}

Ed = Sample Econogreen, d= no of days of aging (2 to 20 days)

K = Rate Constant, s^{-1}

OIT = Oxidative Induction Time

R = Universal Gas Constant, $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

R² = Linear Regression Coefficient

SEM = Scanning

T = Absolute Temperature, K

TG = Thermogravimetry

TGA = Thermogravimetric Analysis

Y = Sample Yaadgar brand

Yd = Sample Yaadgar brand, d= no of days of aging (2 to 20 days)

n = Order of Reaction

t = time, s^{-1}

α = Degree of Conversion

β = Heating Rate, K s^{-1}

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