

The Effect of Photo-Initiated Oxidation on Mechanical Properties of High Density Polyethylene / Linear Low Density Polyethylene Blends

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Abstract

The long – term behaviour of polyethylene products used out doors is affected by weathering. In the present work, weathering test was carried out to find the effect of the environment conditions on the mechanical properties of HDPE/LLDPE blends with different weight percents (0, 15, 30, and 45 %) relative to the LLDPE by increasing the exposure times to (100, 150, 200, 250, 300) hr.

A series of tests (destructive), tensile, impact and hardness were carried out on the prepared samples, the results obtained declare the changes on the material behaviour from ductile to brittle and the polymer shows a decline in the mechanical properties with increasing the exposure times.

In the present work empirical equations were reached which could be used to calculate one of the mechanical properties in terms of exposure time, weight percent of LLDPE content and to other mechanical properties.

Keywords: low density polyethylene, how density polyethylene.

Introduction

The term "weathering" is used by technologists as a comprehensive description of all the possible changes which may occur in polymer on exposure out doors. The main components of the weather which causes degradation are sunlight, temperature, moisture, wind, dust and pollutants. Moisture and humidity can have secondary effects in weathering, the primary process occurring is photo – oxidation or perhaps more accurately photo initiated oxidation; the effect of light is primarily on the generation of free radicals [1].

The sun is the primary cause of most climatic phenomena found on earth. The wave length of the radiation from the sun which reaches the earth's surface extends from the infra – red (> 700 nm), through the visible spectrum (400-700 nm) into the ultra – violet (< 400 nm) with a cut off at approximately 300 nm depending upon atmospheric conditions. The energies of 700, 400 and 300 nm photons are approximately 170, 300 and 390 kJ mol⁻¹ respectively. The strength of C – C

and C – H bonds are approximately 240 and 340 kJ mol⁻¹ respectively although they may be very much less in certain environments [2]. Polymers have different photodegradation sensitivities to UV light of different wave length.

As plastics of increasing durability have been made available, it has become more necessary and at the same time more difficult to predict acceptable service life of specific formulations and products without waiting for actual in use failures to occur. Many polymers show a decline in mechanical properties during service life time (e.g. loss of tensile strength, surface appearance or discoloration) when they are exposed to sunlight and particularly to UV – light. Thus, stabilization of polymers is of great economic importance, the aim of stabilization is to prevent and / or control the processes, which may damage a polymer during its preparation, compounding, processing, or use [3].

Organic materials, both of synthetic and natural origin, readily undergo reaction with oxygen [4]. Oxidation can manifest itself in every stage of the life cycle of a polymer, during manufacturing and storage of

the polymer resin, as well as during processing and end – use of the plastic article [5]. Thus, photo - oxidation degradation of polymers has received considerable interest. In (1967) Blumberg studied the change in mechanical properties of polyethylene, high impact polystyrene, polypropylene and polymethacrylate, based on tensile mechanism, after exposure to artificial weathering [6]. As regards the effect of pollutants on organic polymers, Jellinek (1978) has shown that polyethylene and polypropylene are cross – linked when exposed to Ultra violet radiation in the presence of oxygen and sulphur dioxide [7]. In (1981) Pabiot Jose studied the change in mechanical behaviour of high - density polyethylene, polypropylene and polyvinyl chloride during photochemical aging in which the polymers were exposed for 1700 hours to artificial aging in weatherometer [8]. In (1995)Hokstra, Breen and Audouin studied the UV – stabilized and non UV – stabilized HDPE foils that were photo – oxidized in a Xenotester[9].In (1997) Hoekstra and Spoomaker studied the mechanical behaviour of non UV – stabilized and stabilized HDPE foils as a function of the exposure time and at different straining rates[10].In (2003) Shishan, and Jun , studied the structure properties of high – density polyethylene functionalized by ultraviolet irradiation at different light intensities in air[11]. In this study, the change in mechanical properties of blends of linear low - density polyethylene, LLDPE,with high - density polyethylene HDPE,after exposure to UV light ,are investigated.

Experimental Work

Materials

In this work two types of commercial polyethylene were used, one was the high - density polyethylene (EHM 6003) of a density equal to 0.963 gm/cm³ that was used as a matrix and the other was linear-low-density polyethylene of density equal to 0.94 gm/ cm³.

Methods

The process involves mixing of high-density polyethylene with different weight percent (0, 15, 30, and 45%) of linear-low-density polyethylene using the two roll mills. The mixing machine used for this purpose a roll mill poly mix 150P the mixing machine is operated at a temperature of 135 oC and at speed approximately 10 mm/min. Standard test of all mechanical and environmental properties of the prepared polyethylene blends were carried out. A climatest weather – o – meter type (ERICHSEN) was used to age the samples. The light source of a climatest consists of a cylindrical geometric array of fluorescent tubes, which are arranged in the center of the test chamber and emit radiation similar to

that of natural sunlight. Condensation was produced by exposing the test surface to a heated saturated mixture of air and water vapour. Specimens were mounted on a frame which rotates at 1 rev. / min around the lamp system and the specimens were alternately exposed to ultraviolet radiation and condensation. The tests were done on sets of the HDPE / LLDPE blends with different weight percents (0, 15, 30, and 45) % relative to the LLDPE by exposing the sets of the four types for 300 hours in climatest with 50 % relative humidity and temperature of 40oC, and samples were collected every 50 hours.

Tensile properties, impact resistance and hardness tests were carried out for examining the mechanical properties of exposed and unexposed samples.

Tensile properties were measured by using Instron testing machine. Data on toughness are usually supplied from Izod or charpy impact test, in this work the impact resistance was determined using Charpy impact test instrument No – 43 – 1, made by Testing Machines, Inc., samples were notched (1 mm depth) by using Ceast notch instrument. Brinell method was used to determine the hardness of the polymer materials, a rigid steel ball was used in Brinell test with (5 mm) diameter, and (700N) load was applied at the sample for (15 sec).

Results and Discussion

Tensile Test

The modulus measures the resistance of a material to elastic deformation. Fig.1 shows the modulus of elasticity (E) of the materials as a function of exposure time and at different % LLDPE content. From this figure it is clearly seen, that the increasing of the exposure time from (100) hrs to (300) hrs causes an increase in the modulus of elasticity, this may be due to the fact that increasing the exposing time causes an increase in the chain scission and cross linking due to photo – oxidation degradation.

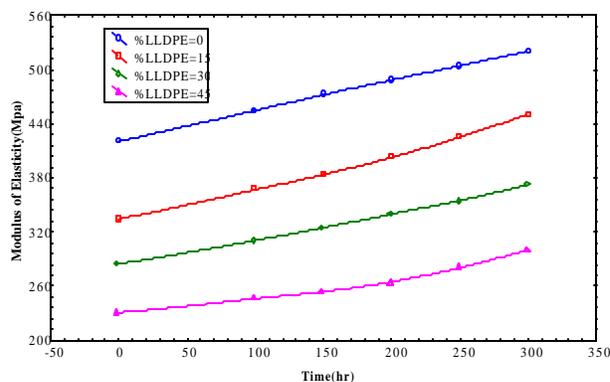


Fig.1 Modulus of elasticity as a function of exposure times at different LLDPE content (wt %).

The tensile strength (σ_u) values (the stress at maximum load) were determined; Fig.2 shows the tensile strength as a function of exposing time and at different % LLDPE contents. It is clear that increasing the exposure time from (100) hrs to (300) hrs leads to decrease the tensile strength, that the polymer shows a decline in mechanical properties when it is exposed to UV – light. Due to chemical reactions, initiated by a U – V quantum and in the presence of oxygen, the long polymer chains can break. If many chains are broken, the polymer is unable to transfer a load effectively and as a result the polymer embrittles.

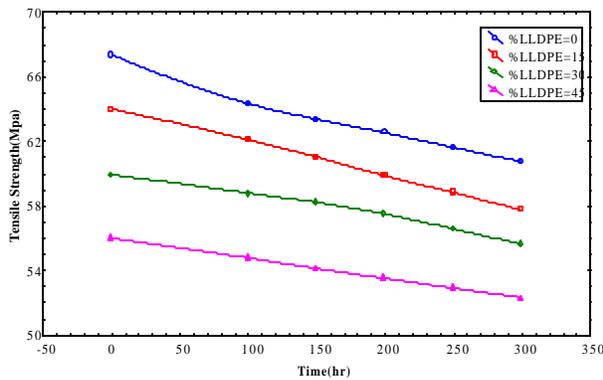


Fig. 2 Tensile strength as a function of exposure times at different LLDPE content (wt %)

Figure (3) shows the tensile strength at break (σ_B) as a function of exposure time and at different % LLDPE contents, from this figure it is clear that the (σ_B) for the neat polymer (HDPE) decreases with increasing exposure time. Samples contained (15, 30 %) of LLDPE were broken as a ductile materials during exposing to ultra violet radiation at exposure time ranging between (0 – 100) hr and for time ranging between (0 – 150) hr for the samples containing 45% LLDPE, that when the load in the tensile test reached a certain level the crack of the specimen propagated in a controlled manner under a gradually increasing total load and opens into a U – notch owing to withdrawing (high plastic extension) of the remainder of the material . Therefore from this figure it is clearly seen that the tensile strength of these blends decrease with increasing exposure time limit of the previous intervals.

The ductile – brittle behavior transition can be seen in blends which contain (15, 30%) LLDPE at (200) hr and at (250) hr for the blends with 45% LLDPE. The samples failed as a brittle material at a stress which was equal to the values of tensile strength, and gradually decreased with increasing the exposure time to (300) hr, this is due to the photo – oxidation degradation which causes a breakdown of the bonds in the polymer chain and cross linking and that leads to decrease the molecular weight and increase the crystallinity, this is the direct cause of mechanical failure.

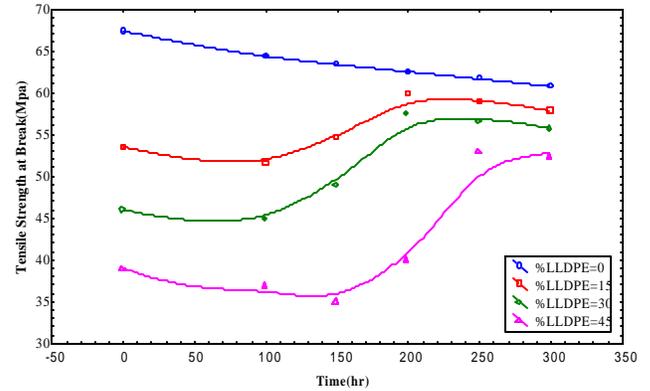


Fig. 3 Tensile strength at break as a function of exposure times at different LLDPE content (wt %)

Elongation is the increase in length of a measured polymer strip, when stretched to the breaking point. It is expressed in terms of the percentage of the original length. Fig.4 shows the % elongation at break as a function of exposure time and at different % LLDPE contents, from this figure it is clear that increasing the exposure time leads to decrease the (ϵ_B) which is attributed to the fact that the polymers show a decline in mechanical properties when they are exposed to UV – light, the crystallinity increases and the material loses its elasticity.

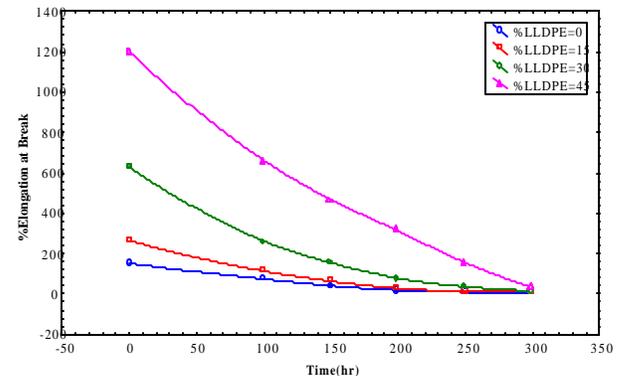


Fig.4 % Elongation as a function of exposure times at different LLDPE contents (wt %).

Impact Test

In view of the surface nature of many weathering processes the degree to which impact properties are affected by exposure to light can be of major importance, Fig.5 shows the impact strength (I) as a function of exposure time and at different % LLDPE contents. It is clear from this figure that the impact strength decreases with increasing the exposure time, this due to the chain scission and cross linkage which occur during exposing

the material to ultra violet radiation, which causes an increase in the crystallinity of the polymer, crystallinity influences its stiffness and toughness, as the crystallinity increases, its flexibility decreases and the polymer's ability to absorb and dissipate energy also decreases [12].

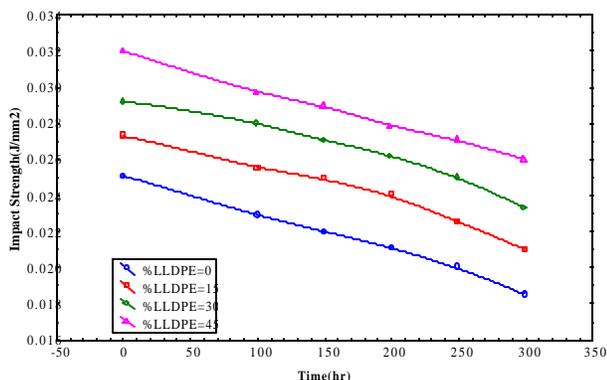


Fig.5 Impact strength as a function of exposure times at different LLDPE contents (wt %)

Hardness

Hardness is commonly defined as the resistance of a material to indentation by a harder material with applied load. Fig.6 shows the Brinell hardness (HB) as a function of exposure time and at different % LLDPE contents. From this figure it is clearly seen that the increase in exposure time leads to an increase in the hardness of the material, this may be attributed to the fact that a strong change in morphology affects the mechanical behaviour of weathered polymers negatively, the molecular weight decreases and the density and crystallinity increases, increasing the crystallinity increases hardness, stiffness, heat resistance, modulus of elasticity and chemical resistance [13, 14].

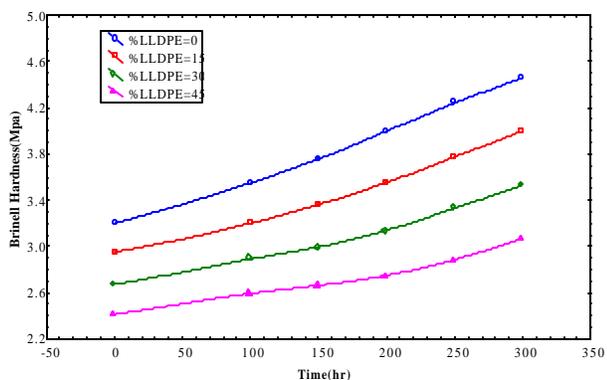


Fig.6 Brinell hardness as a function of exposure times at different LLDPE contents (wt %).

The Analysis of Empirical Correlation

The experimental results of this study are used to develop empirical correlation. The dependent and independent variables were introduced into the computer program in such a way that the developed models could be used for the weathered HDPE / LLDPE blends to find the change in mechanical properties caused by exposing the material to ultra violet radiation. The independent variables, which affect the mechanical properties of the weathered HDPE / LLDPE blends, are weight percent of LLDPE content and the exposure time.

Equations (3.1) to (3.5) as shown in table 1 represent the developed models for the modulus of elasticity, tensile strength, tensile strength at break, Brinell hardness and impact strength with weight percent of LLDPE content and exposure time respectively, the appropriate coefficient is used from table 2. Equation (3.2) has less absolute average error (0.5%). Equation (3.6) as shown in table 3 represents the relation between modulus of elasticity and the combination (exposure time, weight percent of LLDPE, tensile strength, tensile strength at break, elongation at break, Brinell hardness, impact strength). Absolute error is equal to (0.79). Equations (3.6) to (3.10) can be used to calculate one of the mechanical properties depending on the other properties. These equations are in agreement with experimental results. Equation (3.10) has less absolute average error (0.36%) that appropriate coefficient is used from table 4, a correlation between the experimental and calculated results for equation (3.10) is given in Fig. 7.

Statistical analysis for the developed modules is given in tables (1, 3) which include the values of correlation coefficients which indicate that the experimental and model data are in excellent agreement.

Table 1. Equations of the mechanical properties as a function of exposure time and weight percent of LLDPE

Eq. No.	Equations	Correlation Coefficient	AVE %
3.1	$E = a_0 + a_1 t + a_2 C + a_3 tC + a_4 t^2 + a_5 C^2 + a_6 (t/(a_7 + C))$	0.997	2.26
3.2	$\sigma_u = a_0 + a_1 t + a_2 C + a_3 tC + a_4 t^2 + a_5 C^2 + a_6 (t/(a_7 + C))$	0.996	0.5
3.3	$\sigma_b = a_0 + a_1 t + a_2 C + a_3 tC + a_4 t^2 + a_5 C^2 + a_6 (t/(a_7 + C))$	0.945	4.61
3.4	$H_B = a_0 + a_1 t + a_2 C + a_3 tC + a_4 C^2 + a_5 (t/(a_6 + C))$	0.928	3.5
3.5	$I = a_0 + a_1 t + a_2 C + a_3 C^2$	0.995	1.08

Table 2. Coefficient for the equations (3.1) to (3.5)

a	Equation				
	(3.1)	(3.2)	(3.3)	(3.4)	(3.5)
a ₀	412.5717	67.2919	66.8751	3.07577	0.02507
a ₁	0.26748	1.12872	5.71954	-0.12361	-0.00002
a ₂	-2.10919	-0.11522	64.6989	-0.00497	0.000078
a ₃	-0.00205	-0.002085	-0.008092	0.00019	0.000077
a ₄	0.000258	0.000001	0.000121	-0.00497	-----
a ₅	-2.10919	-0.12894	-65.4159	56.5852	-----
a ₆	0.000383	-522.701	-3157.84	441.1564	-----
a ₇	0.009696	453.4866	547.1	-----	-----

Table 3. Shows the relationship between individual mechanical property as a function of other properties and with exposure time and %wtLLDPE

Eq. No.	Equations	Correlation Coefficient	AVE %
3.6	$E = a_0 + a_1 t + a_2 C + a_3 C_a + a_4 C_b + a_5 C_b$ $+ a_6 H_B + a_7 I + a_8 E^2 + a_9 C^2 + a_{10} C_a^2$ $+ a_{11} C_b^2 + a_{12} C_b^2 + a_{13} H_B^2 + a_{14} I^2$	0.9993	0.79
3.7	$C_a = a_0 + a_1 E + a_2 t + a_3 C + a_4 C_b + a_5 C_b$ $+ a_6 H_B + a_7 I + a_8 E^2 + a_9 t^2 + a_{10} C^2$ $+ a_{11} C_b^2 + a_{12} C_b^2 + a_{13} H_B^2 + a_{14} I^2$	0.9994	0.44
3.8	$C_b = a_0 + a_1 E + a_2 t + a_3 C + a_4 C_a + a_5 C_b$ $+ a_6 H_B + a_7 I + a_8 E^2 + a_9 t^2 + a_{10} C^2$ $+ a_{11} C_a^2 + a_{12} C_b^2 + a_{13} H_B^2 + a_{14} I^2$	0.9817	2.44
3.9	$H_B = a_0 + a_1 E + a_2 t + a_3 C + a_4 C_a + a_5 C_b$ $+ a_6 C_b + a_7 I + a_8 E^2 + a_9 t^2 + a_{10} C^2$ $+ a_{11} C_a^2 + a_{12} C_b^2 + a_{13} I^2$	0.9995	0.6
3.10	$I = a_0 + a_1 E + a_2 t + a_3 C + a_4 C_a + a_5 C_b$ $+ a_6 C_b + a_7 H_B + a_8 E^2 + a_9 t^2 + a_{10} C^2$ $+ a_{11} C_a^2 + a_{12} C_b^2 + a_{13} C_b^2 + a_{14} H_B^2$	0.9996	0.36

Table 4. Coefficient for the equations (3.6) to (3.10)

a	Equation				
	(3.6)	(3.7)	(3.8)	(3.9)	(3.10)
a ₀	-650.44	90.3406	-1651.57	-3.9114	0.1008
a ₁	0.20686	0.0256	0.0864	-0.00793	-0.000017
a ₂	-3.02914	-0.606	0.15823	0.002703	-0.000028
a ₃	46.2158	0.1801	-2.809	-0.01804	0.000256
a ₄	-3.92936	0.4106	41.6054	0.21451	-0.01815
a ₅	-0.2152	-0.01598	0.0322	-0.01186	-0.00017
a ₆	228.065	-23.936	22.0824	0.000214	-0.0000082
a ₇	-49454.7	2404.9	20710.25	137.765	-0.00472
a ₈	0.00013	-0.000034	0.000093	0.000012	0.000000012
a ₉	0.24604	-0.000017	0.000664	0.000004	0.00000003
a ₁₀	-0.37635	-0.0019	0.02467	-0.000185	-0.0000016
a ₁₁	0.04545	0.00426	-0.32837	-0.00172	0.0000131
a ₁₂	0.000002	0.000007	-0.000014	0.000087	0.00000199
a ₁₃	-29.3961	4.0528	-9.20609	-2174.14	0.00000004
a ₁₄	850288	-67594.7	-233717	----	----

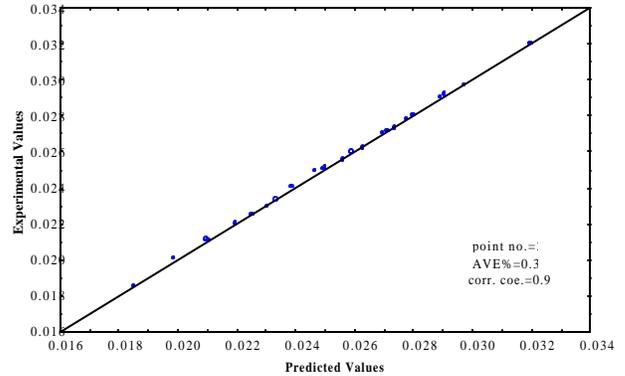


Fig. 7 Experimental versus predicted values for Eq. (3.10)

Conclusions

Results obtained in this work proves that higher exposure times yield higher modulus of elasticity, while increased the exposure times was found to decrease the elongation of the polymeric matrix. Addition of LLDPE to HDPE matrix reduces the tensile strength at break and the higher exposure times (>150hr) the reductions are less pronounced and it seems to be less for a given blend. Increasing exposure times decreases tensile strength, and the higher exposure times seem to reduce the impact strength for all the samples. Hardness values were observed to be the highest in pure HDPE, and these values decrease with increasing LLDPE wt% blend. Moreover, higher exposure times yielded increase in hardness values. In the analysis of empirical correlation of the polynomial equations for modulus of elasticity, tensile strength, tensile strength at break, hardness and impact strength, especially of the high values of the correlation coefficients indicate that the experimental and model data are in excellent agreement.

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