# Studing Of Some Phisical Properties And Morphology Of Blends Of Hdpe /Lldpe After And Before Exposure To Uv Light

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## Abstract

Products made of polyethylene used out doors are subjected to UV-degradation. In fact, many polymers show changes in physical properties during service lifetime, when they are exposed to sun light and particularity to UV-light. In the present work, the physical properties and the morphology of blends of high – density polyethylene (HDPE)/linear-low-density polyethylene (LLDPE) studied before and after exposure to UV –light.

HDPE was mixed with different weight percent (0, 15, 30, and 45%) of LLDPE using the two roll mills; the mixing machine is operated at a temperature of 135 $^{o}$C. Weathering test was carried out to find the effect of the environment condition on the physical properties of the polymeric materials by increasing the exposure times to (100,200,300) hr. The physical properties and the morphology were specified by measuring the (absorption properties, and densities), for the former, and photomicrograph for the latter. The results obtained in this work show that the density of pure HDPE and HDPE/LLDPE blends increased with the increasing the exposure time, and that immersing the HDPE and HDPE/LLDPE blends in water can produce a variety of damage and this damage increased with the increasing of the exposure times also, as the amount of LLDPE is increased in the HDPE/LLDPE blends the amount of water absorbed and diffusivity coefficient, increase greatly, and from the optical micrograph results showed clearly the damage obtained due to exposure to UV light for 300 hr for pure HDPE and HDPE/LLDPE blends.

**Keywords:** HDPE/LLDPE, physical properties, UV light

# دراسة بعض الخواص الفيزياوية والبنية الشكلية لممزوجات HDPE/LLDPE قبل وبعد التعريض للاشعة الفوق بنفسجية

## الخلاصة

ان المنتجات المصنوعه من ماده البولي اثيلين والتي تستخدم في الهواء الطلق او العراء تتعرض ألى ألانحلال نتيجه تعرضها للأشعه الفوق بنفسجيه .ألعديد من ألبوليمرات تشهد تغيراً واضحاً في خواصها الفيزياويه مع مرور الوقت وذلك نتيجه ألتعرض الى أشعه ألشمس وبصوره خاصه ألى ألأشعه فوق ألبنفسجيه.

في البحث الحالي تم دراسه ألخواص ألفيزياويه وكذلك دراسه ألبنيه أو ألشكل لممزوجات من ألبولي أثيلين عالي ألكثافه (HDPE)/ بولي أثيلين واطىء ألكثافه ألخطي(LLDPE) قبل وبعد تعريضها ألى ألأشعه فوق ألبنفسجيه.في بحثنا ألحالي تم مزج ألبولي أثيلين عالي ألكثافه مع نسب وزنيه من ألبولي أثيلين واطىء ألكثافه ألخطي (45,30,15,0٪) وذلك باستخدام ألاسطوانات ألمدلفنه.

تم اجراء فحص التجويه وذلك لأيجاد تأثير الضروف الجويه على المخاليط البوليمريه وذلك بزياده زمن التعريض(100, 200, و300) ساعة.الصفات الفيزياويه والبنيه الشكليه تم تعيينها وذلك بقياس (الكثافه وخواص الامتصاصيه ) وعن طريق التصوير المجهري .النتائج تم الحصول عليها في هذه الدراسه توضح بأن كثافه ألبولي أثيلين ألنقي وممزوجات HDPE/LLDPE تزداد بزياده زمن التعريض للأشعه فوق بنفسجيه, وكذلك عمليه غمس النماذج في الماء قد أدى ألىاحداث أضرار مختلفه وهذه الاضرار تزداد بزياده زمن التعريض,وبزياده النسبه الوزنيه للبولي أثيلين واطىء ألكثافه ألخطي

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في ممزوجات HDPE/LLDPE ,تزداد كميه الماء الممتصه وكذلك يزداد معامل الامتصاصيه بصوره كبيره ,ومن نتائج التصوير المجهري يتضح جلياً مقدار الاذى الحاصل في المواد البوليمريه المحـــضره نتيجه تعرضها للأشعه ألفوق بنفسجيه ولحوالي 300 ساعه.

## 1.Introduction

Modified properties, lower prices and reuse of polymers are needed to meet demands of today's society and therefore of the polymer industry. Plastics are used by almost everybody since (for example) most domestic machines have a housing, which is made out of it [1]. It is estimated that 60 to 70 % of LLDPE enters the market as blends, primarily with other member of the polyolefin family [2]. Unprotected polyethylene and polypropylene react readily with oxygen during exposure and often become brittle long before visual evidence of breakdown appears. It was found that, exposure of unprotected PP and PE to oxygen at elevated temperatures or under ultraviolet radiation produces a rapid rise in crystallinity .The polymer is protected from harmful radiation at the cost of UV absorption, which is destroyed in the process with time. Several types of organic and inorganic UV absorption are developed for this purpose. Almost all inorganic pigments such as iron oxide and titanium oxide absorb UV radiation to a certain extent and provide some degree of protection [3]. With this background, a number of studies on polyethylene-polyethylene blends have been published, Gupta, and co-workers [4] studied the binary blend of (HDPE) and (LLDPE) in the range of composition from 100% HDPE to 100% LLDPE. Tensile properties (initial modulus, yield stress, and elongation-at-yield, ultimate tensile strength and elongation-at-break, and work of yield and work of rupture) and flexural properties (flexural modulus and flexural yield stress) were studied as a function of blend composition. Karbashewski and Kale [5] studied the effect of additions of (HDPE) on the processability of the (LLDPE), and is found that it is not only that high – molecular – weight characteristics of the high – density portion but also the linear nature of the molecules that have negative effect on processability. Also Gupta and co-workers [6] studied the flexural and impact properties of binary blends of (HDPE) and (LLDPE), over a full range of blending ratios, is presented the impact strength variation of this blend is found to correlate with the variation of the fraction of amorphous phase in the blend. Rana [7] studied the effect of co-crystallization on kinetic parameters of HDPE/ LLDPE blend. Bischel et. al. [8] studied blends of LLDPE and HDPE using the atomic force microscope. From the results, the relative modulus of crystalline regions is observed to increase with increasing HDPE content. Lee and Denn [9] studied the thermal properties of binary and ternary blends of (HDPE), (LDPE) and (LLDPE) in the melt and solid state and found that HDPE / LLDPE blends are homogeneous in the melt and in both crystalline and amorphous regions in the solid state, and exhibit a single melting peak. kyucheol et.al. [10] studied the rheological and mechanical properties in LLDPE/ LDPE, LLDPE/ HDPE, and HDPE/LDPE blends, and they found that all three blends were miscible in the melt, but the LLDPE/LDPE and HDPE/LDPE blends exhibited two crystallization and melting temperatures melt. The melt strength of the blends increased with increasing molecular weight of the LDPE that was used. The mechanical properties of the LLDPE/LDPE blend were higher than calculated from a simple rule of mixtures, while those of the LLDPE/HDPE blend conformed to the rule of mixtures, but the properties of HDPE/LDPE were less than the rule of mixtures prediction. On other hand Rana [11] studied the tensile properties and morphological characteristics of binary blends of the (HDPE) and (LLDPE), and she found that the mechanical properties remained invariant in the 10-90% LLDPE content. The melting endotherms and the crystallization exotherms of these blends are singlet in nature. Also Dr.Najat and Nabeela studied the change in mechanical properties (tensile, impact and hardness properties) due to photo oxidation degradation of HDPE/LLDPE blends (send for publication) .In this study, the morphology and corresponding physical properties (absorption properties, and densities)of blends of HDPE/LLDPE, after and before exposure to UV light, are investigated.

## 2.Experiment

### 2.1 Materials

The neat polymers used in this study are a commercial high – density polyethylene, HDPE type (EHM 6003), that was used as a matrix, and linear – low – density polyethylene, LLDPE type 21018(461). Thermoplastic resins used in present work were locally manufactured in Petrochemical Complex (Basrah-Iraq). The important characteristics of the materials are given in table 1.

### 2.2 Procedure

Blends of HDPE/LLDPE were made by mixing HDPE with various compositions (0, 15, 30, and 45) % of LLDPE using two roll mills. The mixing machine is operated at a temperature of 135 $^{o}$C and at speed approximately 10 mm/min. The mixing machine used for this purpose a roll mill poly mix 150P.Compression moulding was carried out in an electrically heated press (Cininnatic; an hydraulic type of compression moulding machine) the applied pressure was (10 Mpa) and the temperature was 135$^{o}$C.

Standard tests of all physical and environmental properties of the prepared polyethylene blends were carried out, a climatest weatherometer type (ERICHSEN) was used, 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 40$^{o}$C, and samples were collected every 100 hours, 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. Exposing the test surface to a heated saturated mixture of air and water vapour produced condensation. 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.

In order to determine the diffusion coefficient, all the specimens were placed in the water, absorption tests were conducted at temperature range (100 ±2) $^{o}$C and the room temperature is 35 $^{o}$C .The weight of all specimens was determine before they were put in the water (m1), after that the specimens were immersed in water at (100 ±2) $^{o}$C after three hours, then the specimens reweighed (m2) and this step was repeated to determine m3, m4. Then the variations in weight gain (mt) as a percentage of the original dried specimens were determined, and from Fik's second law, diffusion coefficient can be determined. The densities of all specimens were determined; density of test specimens was measured in accordance with ASTM D 792-86, method B. Several samples were taken from each material type .The dry weight of each sample was measured on an electronic balance, then the samples were weighed, and then submerged in ethanol alcohol; excess ethanol on the surface of the samples was removed before weighing. The morphology evaluation was carried out using an optical microscope Nikon 540x. A small specimen was cut from the molded film of the pure HDPE and HDPE/LLDPE at different ratio of LLDPE and different exposure times.

## 3 Results and Discussion

### 3.1 Density Test

Figure 1 shows the density of HDPE/LLDPE blends as a function of % LLDPE content and at different exposure times.

From this figure it is clear that there is a pronounced effect of addition of LLDPE at different weight percents ranging between (15-45) wt. % on the density of the material, LLDPE have a density lower than HDPE so increasing the amount of LLDPE in HDPE /LLDPE blends leads to decrease in the density.

Figure 2 shows the density of HDPE/LLDPE blends 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 density of the material, this may be due to the chain scission and cross linkage which occur during exposing the material to ultra violet radiation, which causes decrease in the molecular weight and increase in the crystallinity of the polymer, and this leads to increase the density [12].

### 3.2 Water Absorption Test

The percentage weight change was defined as:

$$\text{Weight change (\%)} = \frac{(\text{Weight of wet specimen} - \text{Weight of dry specimen})}{\text{Weight of dry specimen}}$$

Figures (3-6) shows the variation in weight gain, Mt, as percentage of the original dried specimen weight, with the square root of time, t, for HDPE/LLDPE blend at different exposure time .The choice of $\sqrt{t}$ as the abscissa was made as Fickian behavior predicts an initial linear relationship between Mt (%) and $\sqrt{t}$. The initial part of the curve was indeed found to be line and the rate of water uptake (the initial gradient of the curves) decrease with exposure time.

From this figure it is clearly seen, that the increasing of the exposure time from (100) hrs to (300) hrs causes decrease in the absorption percent, 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.

An acceleration of water uptake was observed and an eventual reduction the weight of specimens. The results indicated increase degradation in the form of chain scission and HDPE/LLDPE debonding and matrix cracking which allowed greater infiltration of water followed by leaching of the matrix leading to a loss of weight.

The decrease in molecular weight due to chain scission will cause an increase in the crystallinity due to the ability of the short chains to be incorporated in the crystalline, as crystallinity increase, the resistance to gas and moisture vapor permeation, chemical resistance increase [13, 14].

Figures (7-10) shows the variation in weight gain, Mt, as percentage of the original dried specimen weight, with the square root of time, t, for HDPE/LLDPE blend at different weight of LLDPE ranging between (0-45) %wt. The rate of weight change increased linearly for the first (14) hours, it then decreased, the absorption percent was increased with increase the LLDPE content, witch decrease the ability of polymeric material to bearing water during service life. Water absorption causes swelling of the polymer and also acts as politicizing factor. Swelling of the resin due to the presence of the water provoked deformation in the resin rich zones so that the weakened interfaces in the neighborhood of these zones were subjected to greater stresses and were therefore more likely to fail. The amount of water absorbed will depend primarily upon the chemical nature of the polymeric matrix and the environment to which it exposed [15].

The rate at which a material absorbs water is expressed by the diffusion coefficient. Although the diffusion coefficient is not a direct measure of mechanical deterioration, it is a relative measure of the rate at which the material absorbs water and the mechanical properties deteriorate.

The relationship between weight gain and diffusivity during initial water uptake for Fickian diffusion is given by: -

$$D = \pi \left( \frac{Kb}{4M_\infty} \right)$$

Where D=diffusion coefficient (m²/sec).
K=the slop of the curve of $\sqrt{t}$ with weight gain (%).
b=sample thickness (m)
$M_\infty$=max. variation in weight gain

Water was absorbed not only by the mechanism of Fickian diffusion but by other mechanism as well. The importances of these additional mechanisms depend greatly on the exposure time, LLDPE content and duration of immersion. Two factors seen important in trying to understand these phenomena: the presence of the HDPE/LLDPE interface should be considered as third phase and channel for water penetration. Secondly the possibility of water molecules reacting chemically or being fixed physically to the molecular structure of the matrix must be considered.

Figure 11 shows the diffusivity coefficient as a function of LLDPE content (wt %) and at different exposure times. from this figure it is clear that increasing of %LLDPE content lead to increasing the diffusivity coefficient of the material, the slight discrepancy among these values are due to differences in the LLDPE content and bonding between LLDPE and matrix.

Figure 12 shows the diffusivity coefficient of the materials as a function of exposure times and at different LLDPE content (wt %). From this figure it is clear that increasing the exposure time leads to decrease the diffusivity coefficient.

### 3.3 Morphology

Figure 13 shows the optical micrograph of high-density polyethylene/linear-low-density polyethylene blends obtained after melt in the two-roll mill at 135 °C at different blending ratios; the light and dark regions correspond to HDPE and LLDPE respectively. It is seen from figure 13 that HDPE (white) form the continuous phase and LLDPE (black) forms the dispersed phase for HDPE/LLDPE.

Exposure to UV light for 200 hr and less was found to provoke considerably less damage than that produced when exposed to 300 hr fig.14 shows the HDPE and HDPE/LLDPE after 300 hr in UV light.

## 4. Conclusions

Blends of HDPE and LLDPE have been studied, the results obtained in this work showed that increasing the amount of LLDPE in HDPE/LLDPE blends leads to decrease in the density also, the density of pure HDPE and HDPE/LLDPE blends increased with the increasing the exposure time from (0 to 300) hr. The increase in density is due to the chain scission and cross linkage which occurring during exposing the material to ultraviolet radiation, and also from the results presented here indicate that immersing the HDPE and HDPE/LLDPE blends in water can produce a variety of damage. The distribution of the water, and rate at which it is absorbed, depend greatly on the weight percent of LLDPE on the exposure times. As the amount of

LLDPE is increased in the HDPE/LLDPE blends the amount of water absorbed and diffusivity coefficient, increase greatly. Also increasing he exposure times from (`100) hr to (300) hr causes decrease in the absorption percent and the diffusivity coefficient. Further, optical micrograph results showed the damage obtained due to exposure to UV light for 300 hr for pure HDPE and HDPE/LLDPE blends.

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**Table 1.characteristics of neat polymers**

| Property | LLDPE | HDPE |
|---|---|---|
| DENSITY (gm/cm³) | 0.93 | 0.963 |
| MELTING FLOW INDEX(gm/10 min) | 2 | 0.36 |

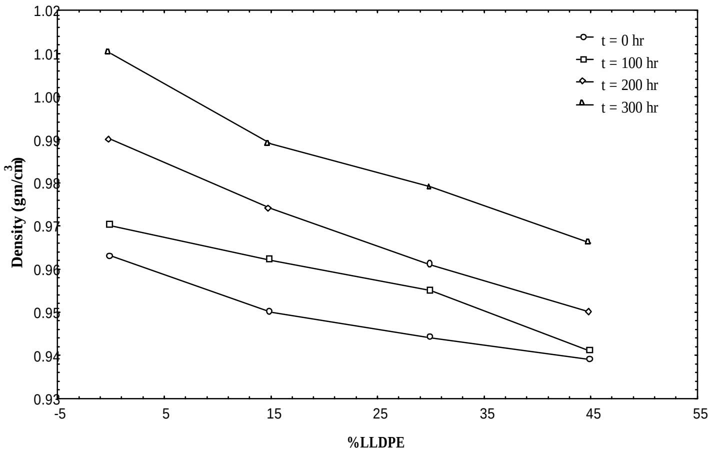


**Fig.1 The density of HDPE/LLDPE blends as a function of LLDPE content (wt %) at different exposure times.**

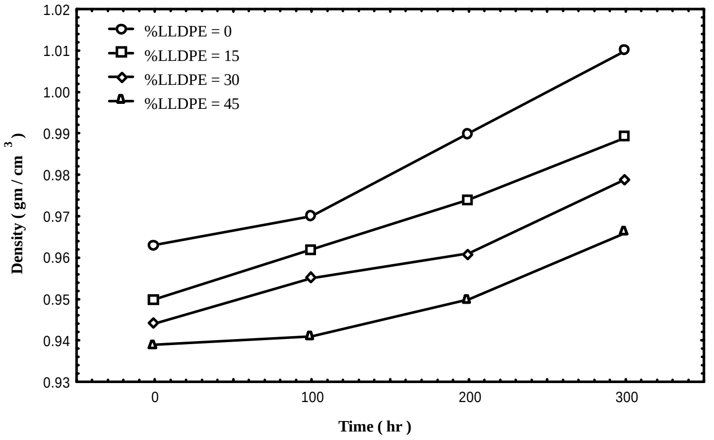


**Fig. 2 The density of HDPE/LLDPE blends as a function of exposure times at different LLDPE content (wt %).**

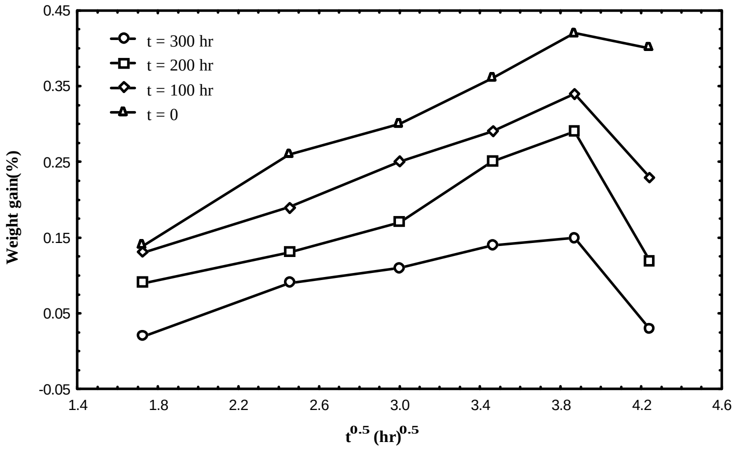


**Fig. 3 The variation in weight gains with the square root of time for HDPE at different exposure times.**

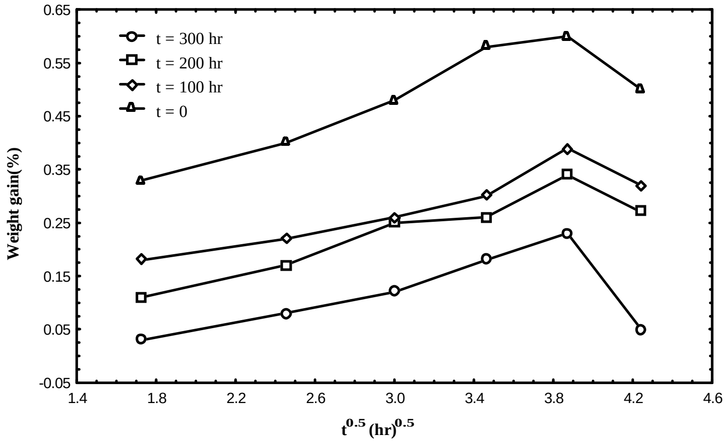


Fig. 4 The variation in weights gains with the square root of time for HDPE/LLDPE blend at different exposure times and at constant LLDPE content (15) wt%.

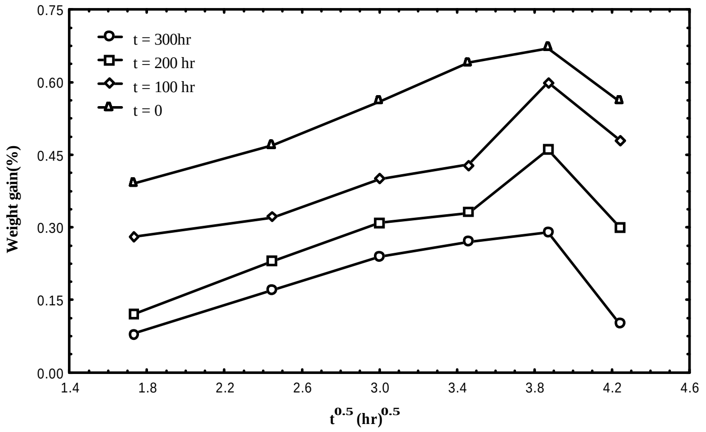


Fig. 5 The variation in weights gains with the square root of time for HDPE/LLDPE blend at different exposure times and at constant LLDPE content (30) wt%.

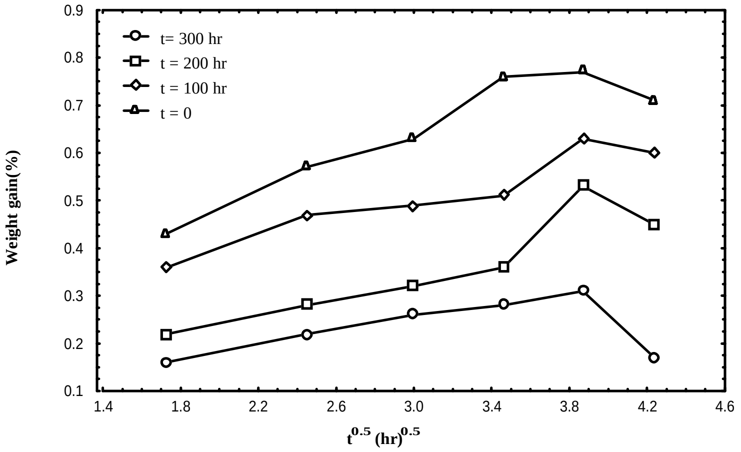


Fig. 6 The variation in weights gains with the square root of time for HDPE/LLDPE blend at different exposure times and at constant LLDPE content (45) wt%.

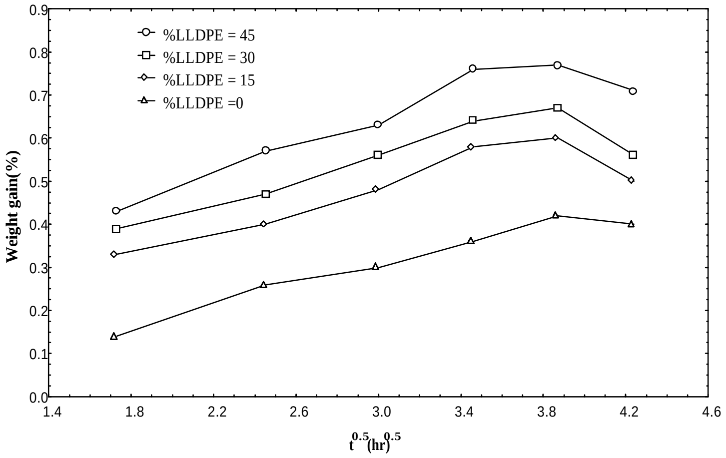


**Fig. 7 The variation in weights gains with the square root of time for HDPE/LLDPE blend at different LLDPE content before exposure to UV light.**

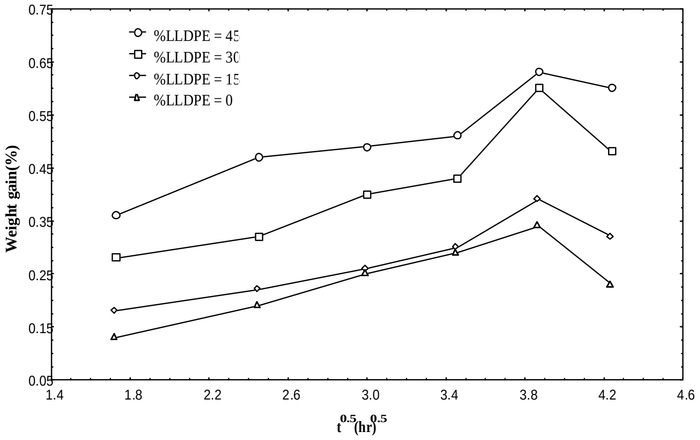


**Fig. 8 The variation in weights gains with the square root of time for HDPE/LLDPE blend at different LLDPE content after (100 hr) of exposure to UV light.**

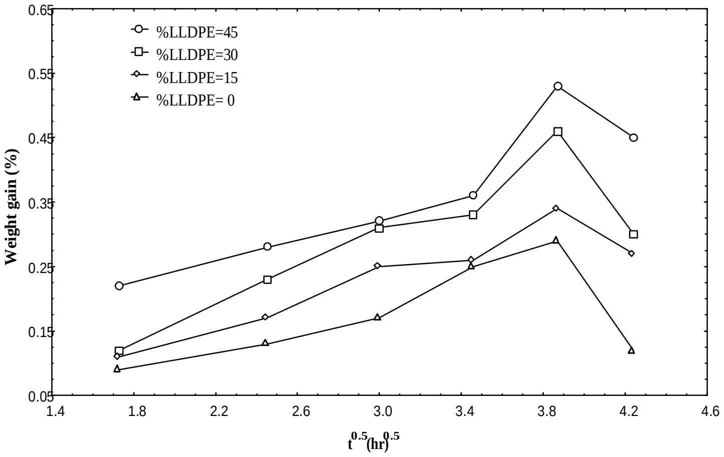


**Fig. 9 The variation in weights gains with the square root of time for HDPE/LLDPE blend at different LLDPE content after (200 hr) of exposure to UV light.**

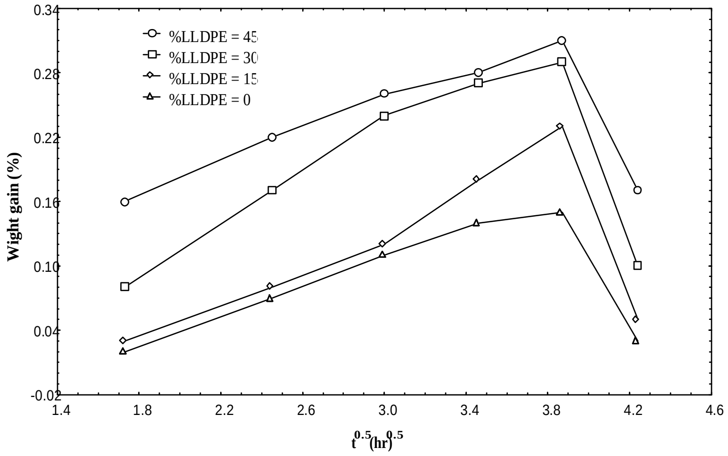


**Fig. 10 The variation in weights gains with the square root of time for HDPE/LLDPE blend at different LLDPE content after (300 hr) of exposure to UV light.**

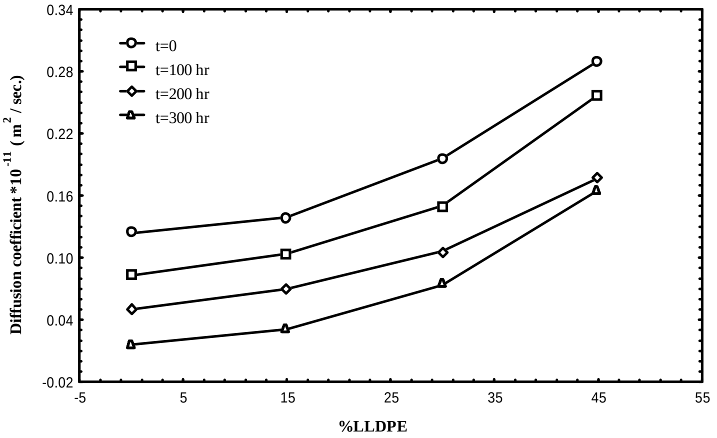


**Fig.11 The diffusivity coefficient of HDPE/LLDPE blends as a function of LLDPE content (wt %) at different exposure times.**

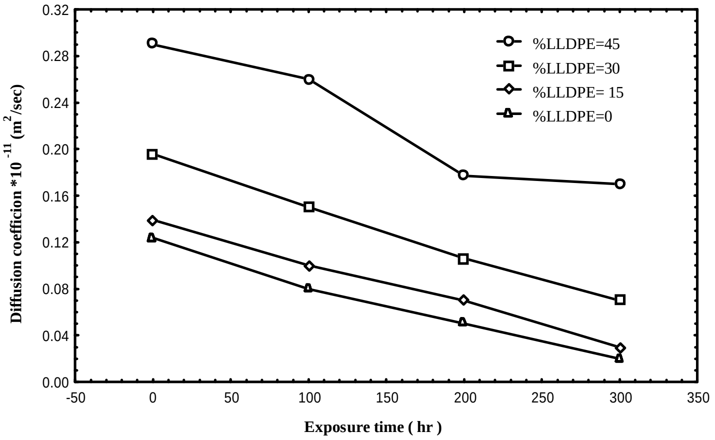
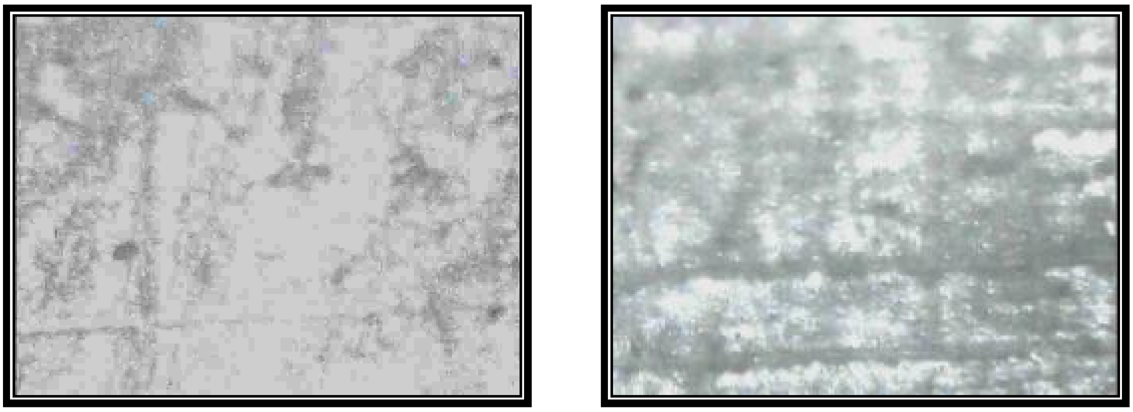
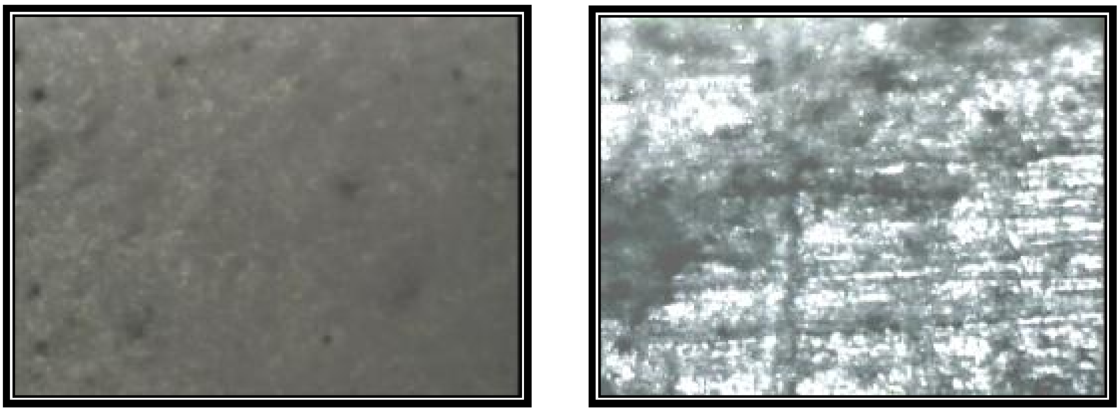


**Fig. 12 the diffusivity coefficient of HDPE/LLDPE blends as a function of exposure times at different LLDPE content (wt %).**



(a) (b)

**Fig.13 Micrographs of (a) pure HDPE and (b) for HDPE/LLDPE blend with 45% LLDPE content before exposure to UV light.**



(c) (d)

**Fig.14 Micrographs of (c) pure HDPE and (d) for HDPE/LLDPE blend with 45% LLDPE content after300 hr of exposure to UV light.**