A Study the Effect of UV Light on Pigmented and Unpigmented LDPE

Dr.Najat J.saleh* & ZanaibY.shnean*

Abstract

In the present work, specimens of polymeric composites were prepared from LDPE with different wt% of TiO_2 and Fe_2O_3 using a single screw extruder which operated at a temperature of (150-170) C^o. Results obtained reveal that after the addition of 7% of TiO_2 to LDPE, some of mechanical properties improved for example tensile strength increased from (18.50)MPa to (28.12) MPa tensile at break increased from (14.96) MPa to (26.02) MPa, modulus of elasticity increased from (63) MPa to (193.98) MPa, hardness increased from (48) to(75),while impact strength decreased from (0.18) to (0.02). After the exposure to UV light all mechanical properties declined but pigment LDPE still has higher mechanical properties unpigmented LDPE. Empirical equations were reached which could be used to calculate one of the mechanical properties in terms of exposure time, weight percent of pigment content and other mechanical properties.

Keywords: composite material, low-density polyethylene, pigment, weathering

دراسة تاثير اشعة فوق البنفسجية

(على البولي الاثلين الواطئ الكثافةعند اضافة الاصباغ وبدونها)

الخلاصة

تم في البحث الحالي تم تحضير مواد متراكبة ذات أساس بوليمري من البولي اثلين الواطئ الكثافــة وأضيفت إلية نسب مختلفة من اوكسيد الحديد وثنائي اوكسيد التيتانييوم وتــم التحــضير باســتخدام الباثقــة الأحادية والتي تم تشغيلها عند الدرجة الحرارية التي تتراوح مابين(170 - 150). اطهرت النتائج التــي تــم الحصول عليها بعداضافة نسبة مثلا 7% من اوكسيد التيتانييوم تحسن العديد من الخواص الميكانيكية كقوة الشد حيث ازدادت من (18.50) إلى (28.12) ميكاباسكال وقوة الشد عند القطع حيث ازدادت من (26.02) (14.96)ميكاباسكال ومعامل المرونة من   (63) إلى (193.98) وكذلك الحال بالنسبة للصلادة حيــث ازدادت من (48 إلى (75) في حين لوحظ انخفاض قوة الصدمة من (0.18) إلــى (0.02) ولأجــل التعرف على تأثير ظروف التجوية على النماذج المحضرة.وقد تم تعريض النماذج للأشعة فــوق البنفــسجية ولازمان مختلفة تتراوح بين (0-250) ساعة.لوحظ انخفاض الصفات الميكانيكية اعلاة مع ملاحظــة ان النماذج المعالجة بالصبغات تمتلك صفات أعلى من تلك الغير المعالجة بالصبغات . وفي البحث الحالي أيضا تم إيجاد معادلات تجريبية يمكن استعمالها لإيجاد قيمة احد الصفات الميكانيكية بدلالة زمن التعرض.النــسبة المئوية لمحتوى البولي اثلين الواطئ الكثافة وبدلالة الخواص الميكانيكية.

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1. Introduction

Low-density polyethylene (LDPE) is produced by the polymerization of highly purified ethylene at very high pressure in the presence of a trace of oxygen. It is flexible and has a lower maximum temperature range than high-density polyethylene [1]. Some important mechanical and thermal properties of low density polyethylene in many practical applications may be lost due to weathering, which harms the surface of (LDPE) and attacks it with photo-oxidation [2]. Most materials are subject to weathering, synthetic polymers offer an impressive range of attractive properties and in many of their applications they are exposed to the outdoor environment [3].The deterioration of a material depends on how and to what extent it interacts with its surroundings [2].The main components of the weather which cause degradation are sunlight, temperature, moisture, wind and pollutants. The light absorption by polymer can be decreased by using some pigments in which many pigmented polymers reverse the light, hence few free radicals will be formed [4], and they generally have a higher density and lower oil absorption, and provide better weathering resistance . The iron oxide that is used in many filler applications absorbs the UV rays and can be used as active container for free radical [5]. Titanium dioxide used to prevent the breaking and cracking operates as active material [6]. Titanium dioxide has the higher weathering resistance and higher light fastness. Rutile grades have a more compact crystal lattice, higher weathering resistance and higher light fastness than in case of anatase [7]. It is well established that photo-oxidation reaction plays an important role in the degradation process of the UV. **Howard and Gilroy** [8], studied the natural and artificial weathering of low-density polyethylene when exposed to the elements for very long times they compared results with these from samples of the same material subjected to artificial "weathering" in modified carbon arc machine. **Dills** [9] studied the effect of TiO_2 on the weathering of polyolefin and noted that "properly selected titanium dioxides can improve rather than harm the weatherability of Polyolefins. **Vzelmeier** [10], studied the effect of pigments such as (pigment red, pigment blue and pigment white) on UV light on the stability of both stabilized and unstabilized PE. **Lind**[11], has shown how the weathering stability of LDPE is affected by the pigment. It was found that pigments used improve the stability of LDPE to various degrees. **Winslow.**[12], showed that the deteriorating influence of sunlight increased from winter to summer and that it was due to the

shortest wavelengths of solar radiation that causes the deterioration in LDPE. **Ogbabe and Ossai**[13], studied the effect of color on the mechanical and chemical properties of photo-oxidized PE. **Angulo and Sanchez. [**14], studied the effect of photo-degradation of low-density polyethylene films formulated with titanium dioxide pigment. **Salem** [15], studied the mechanical properties of UV-irradiated low-density polyethylene with carbon black and titanium dioxide. In this work a mixture of TiO_2 and Fe_2O_3 in different formulations was added to a locally produced LDPE to improve its properties. After it was exposed to UV light, the mechanical properties of LDPE has been investigated.

2.Experimental
2.1 Materials
Two main types of materials were used;first was the LDPE of a density of 0.9235 gm/cm^3 and grade number(21018 **461**) **,**that was used a matrix , and second was the inorganic pigment (TiO_2 and Fe_2O_3), the TiO_2 used in this present work is rutile; and the Fe_2O_3 used in this present work is hematite .

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2.2 Method

The single-screw extruder machine is used to mix raw materials (LDPE and pigment).The compounding process involves mixing of different weight percents of LDPE and inorganic pigment. The mixing machine (extruder)was operated at temperature between $(150-170)^{o}C$ and rotation increased from(0-60)r.p.m.The compounding time involved was less than(5 min). After compounding process was completed (i.e., the melt became homogenous),the homogenous mixture was then pressed in the hydraulic press by applying temperature and pressure at the same time, the temperature was applied to the upper and lower sides of mold while the sample was still under the applied pressure of . (10MPa) and

temperature of $(150\ ^{0}C)$ for a (5min). A sheet with dimension (290x 205x4) mm was obtained. A climate test was carried out using weather meter type (Erichsen) type with intensity of 13.5 w/m^2 which gives a light with a wave length of 305 nm. The test was carried out on a set of

LDPE with different of formulations as shown in Table (1) for 250 hours and samples were

collected each 50 hours.

In the present work, a series of standard tests (destructive), tensile, impact, hardness, and modulus of elasticity were conducted. Tensile strength was measured by using Zwick tester according to ASTM D638[16].Charpy instrument was used to determine the impact test according to the ASTM (D256-87)[16].Shore hardness was used to determine the hardness of the materials. Three point bending tester was used to determine the modulus of elasticity. The ratio of span to depth is (32:1) according to the standard specification of ASTM (D790m-86) [17].

3. Results and Discussion:

3.1Tensile Test: -

Figure.1 shows the tensile strength as a function of exposure time and at different wt

% Fe_2O_3contents. Figure 2 shows the tensile strength as a function of exposure time and at different % TiO_2 contents. From Figures 1-2 it is clear that pure LDPE has lower tensile strength while pigmented LDPE with TiO_2 and Fe_2O_3 has higher tensile strength. Actually tensile strength increased from (18.50) MPa to (28.12) MPa when the amount of TiO_2 increased from zero to 7 wt%. After exposure to UV light it is clear that increasing the exposing time from (0-250) hrs leads to decrease in the tensile strength but still the decrease in pigment LDPE tensile strength is lower than that of pure LDPE This is due to the photo-oxidation degradation, which causes a breakdown of chemical bonds, resulting in embitterment and also increased cross linking and chain scission, which lead to shrinking and crack [3]. Thus pure (LDPE) shows rapid loss of tensile strength but the addition of pigment such as (Fe_2O_3 and TiO_2) can improve its performance [7]. This result is in good agreement with result obtained by Salem [15]. The values of tensile strength at break were determined; Figure (3) illustrates the relation between tensile strength at break and exposure time to UV-light and at different % of Fe_2O_3. Fig. (4) illustrates the relation between tensile strength at break and exposure time to UV-light and at different % of TiO_2.From Figures (3 and 4) it is clearly seen that the tensile strength at break value decreases with

increasing time of exposure to UV –light at different wt% pigments ($TiO_2$and Fe_2O_3). Tensile strength at break for pure LDPE is much lower

than pigment LDPE and the decreases in tensile strength of pigment LDPE is lower than pure LDPE. These results agree well with Salem's [15], who found that the decrease in molecular weight due to chain scission causes an increase in the crystallinity and by oxygen uptake the increase in crystallinity is closely related to the decrease in tensile strength at

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break.
Figure 5 shows the %elongation at break as a function of exposure time at different wt. % of

TiO_2. Figures 6 show the %elongation at break as a function of exposure time at different wt% of Fe_2O_3. From Figures 5 and 6 it is clearly seen that increasing the exposure time leads to decrease in the (ζ_B) when the material is exposed to UV-light also it is clear from both figures that the virgin LDPE has a higher %elongation than pigment LDPE. One reason why polymers are so susceptible to radiation is their long chain structure. Because of their high molecular weight, typically of the order of several thousand-carbon atoms, a relatively small number of radiation events affect a high proportion of the molecules. Consequently, a relatively small amount of radiation can produce a large change in the average molecular weight. The primary effect of radiation is to excite the electrons from the chemical bonds,provided the lifetime of the excited bond is greater than that of thermal vibration within the material, either main chain rupture or side chain rupture can occur. If these broken bonds recombine, the material is left unaffected. However, in a proportion of the events the bonds no longer recombine but combine with other bonds leading to an altered structure. The broken bond, a radical or ion, can be a very reactive species. Therefore, from figures it is clearly seen that elongation at break of the composite decreases with increasing exposure time. [5, 8].

3.2 Impact Strength
Fig.7 shows the relation between the impact strength as function of exposure time and at different % TiO_2 contents. Fig.8 shows the relation between the impact strength as a function
of exposure time and at different % Fe_2O_3 contents. It is clear from these figures that the impact strength decreases with increasing the exposure time. This is due to

the cross-linking and chain scission process occurring during photo-oxidation degradation, cross linking which is the joining together of two molecules, converts the solid from a flexible extensible material to a more brittle material [3]. Chain scission, on the other hand, can convert the solid from a hard rigid solid through a waxy state, also increase of exposure time to UV-light which causes an increase in the crystallinity of the polymer, and this leads to decrease in its toughness [8].

3.3 Hardness Test
In the present work Durometer hardness type (shore –D) was used to measure the hardness. Figure 9 illustrates the relation between hardness test as a function of exposure time and at different %TiO_2 contents. Figure 10 illustrates the relation between hardness test a function of exposure time and at different wt% Fe_2O_3 content. From these figures (9and 10) it is clearly seen, that the increase in exposure time leads to an increase in the hardness of the material. These Figures indicate, that the addition of pigment to LDPE causes a decrease in elasticity and increase in the matrix resistance to the indentation compared with pure LDPE.thus, it can be concluded that addition of pigment to LDPE causes improved hardness of LDPE when they are exposed to UV- light compared with pure LDPE. These results are in a good agreement with the result obtained by Salem [15].

3.4 Bending Test
Fig.11 shows the relation between modulus of elasticity and exposure time to UV-light and at different wt% of Fe_2O_3. Fig .12 shows the relation between modulus of elasticity and exposure time to UV-light and at different of wt.% of TiO_2. From Figures 11 and 12 it is clearly seen that the modulus of elasticity (E) value increases with increasing time of exposure to UV-light. This due to the fact that increasing the exposure time leads to an increase in the chain scission and

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cross linking due to photo- oxidation. Cross linking and chain scission processes occurring in Photo-oxidation in LDPE are believed to be sources of great importance in causing changes in the mechanical properties of this material. Due to chain scission and the consumption of oxygen, the molecular weight decreases and the crystallinity and the density increase, also the long polymer chain can break. From the results it can be concluded that after (250) hr of exposure to UV-light all materials failed in brittle manner and their lose elasticity, in addition they have to increase in the degree of crystallinity directly correlated to an increase in modulus.

4. Empirical Correlation Analysis

The results obtained from the experiments in this study are used to develop an empirical correlation for each case (Modulus of elasticity). A statistical software program was used, on a high-speed personal computer (Pentium 4), to help us in the statistical analysis. The manner of developing the present model is by assuming equations of different forms in the computer program, then the calculated values (predicted) of the dependent variable (Y) are compared with the actual values (observed) which are obtained from experiment, and this procedure is repeated until an excellent agreement between the observed and the predicted values is reached. Equations (1) and(2) as shown in Table (2)represent the developed models for modulus of elasticity, with wt% of TiO_2 and Fe_2O_3 exposure time respectively, the appropriate coefficient is used from Table (3).The result can be represented in terms of contour plot as shown in Figures (15)for TiO_2 and (16)for Fe_2O_3 respectively, these figures represent . The relationship between modulus of elasticity, exposure time and wt% of filler, so knowing the value of wt% of filler we can calculate the modulus of elasticity at any exposure time.

5. Conclusions

The experimental results obtained from this lead to the following conclusions:

1- Increased the exposure times was found to increase the modulus of elasticity and increase shore hardness of composite material.

2- Increasing exposure times decrease tensile strength, tensile strength at break, elongation at break and the higher exposure times seem to reduce the impact strength for all samples.

3- In the analysis of empirical correlation of the polynomial equation for modulus of elasticity, especially of the high values of the correlation coefficients indicate that the experimental and

model data are in excellent agreement.

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Table (1) LDPE with different formulation of pigments

Formulate no	Fe_2O_3 %	TiO_2 %
1	2	7
2	4	7
3	6	7
4	7	7
5	7	2
6	7	4
7	7	6
Unformulated.	_	_

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**Table (2) Equations of the mechanical properties as a function of
exposure time and Wt.% of TiO_2 and Wt. %of Fe_2O_3**

Eq.N0	Equations	Correlation coefficient	AVE%
1	$E_T = b_0+b_1t+b_2C+b_3tC+b_4t^2+b_5C^2+b_6(t/(b_7+C))$	0.972	4.028
2	$E_F = b_0+b_1t+b_2C+b_3tC+b_4t^2+b_5C^2+b_6(t/(b_7+C))$	0.9613	2.239

Table (3) coefficient for the Equations (1) and(2) for TiO_2 and Fe_2O_3

b	Eq. 5.1	Eq. 5.2
b_0	100.0054	13.844
b_1	0.032556	0.1324
b_2	4.048223	1.4039
b_3	0.005378	-0.000553
b_4	-.000465	-0.00524
b_5	-.803974	-0.19695
b_6	0.073858	-0.000325
b_7	2.458936	0.026018

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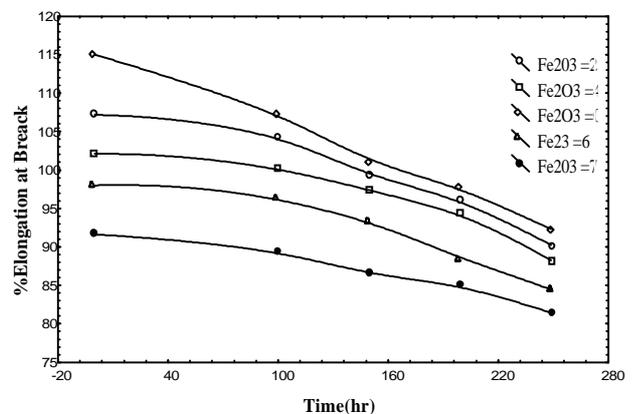and unpigmented LDPE
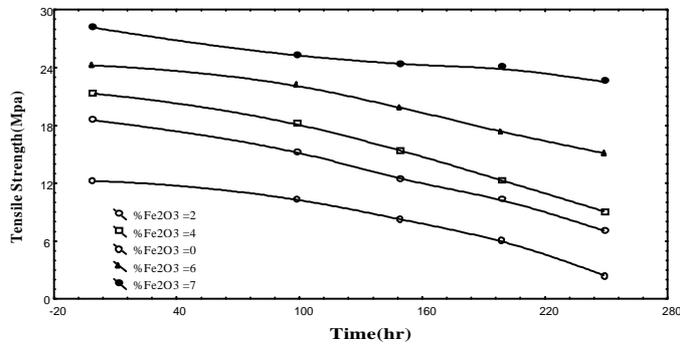
**Figure1 Tensile strength of LDPE as function of
exposure times at different wt% of Fe₂O₃ and constant
TiO₂ content.(7% wt).**
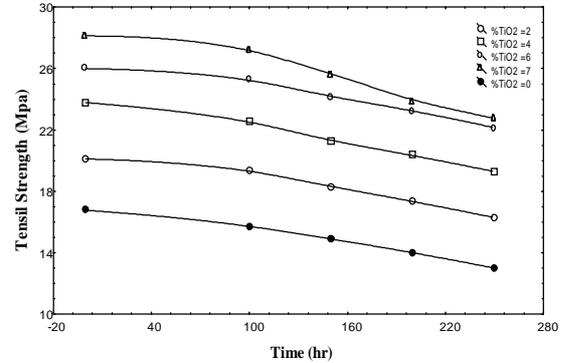
**Figure 2 Tensile strength of LDPE as function of
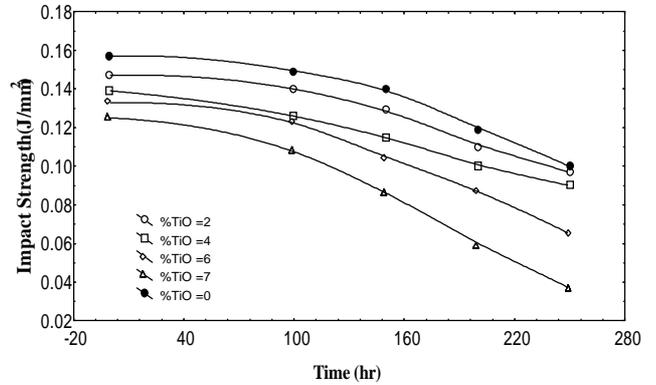exposure times at different wt.% of TiO₂ and constant
Fe₂O₃ content.(7% wt).**
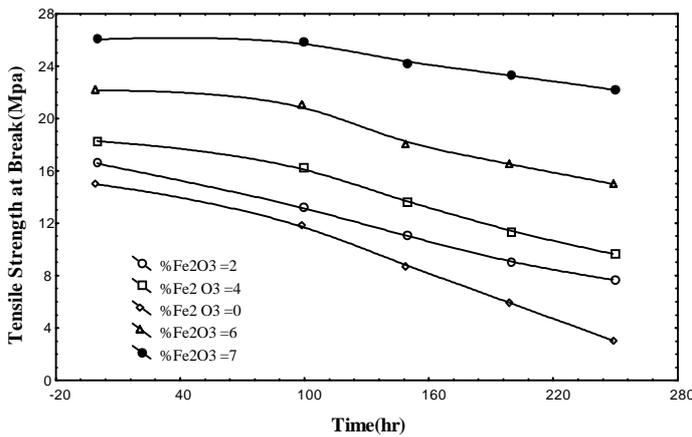
**Figure 3 Tensile strength at break of LDPE as a function of
exposure times at different wt.% of Fe₂O₃ and constant TiO₂
content (7% wt).**
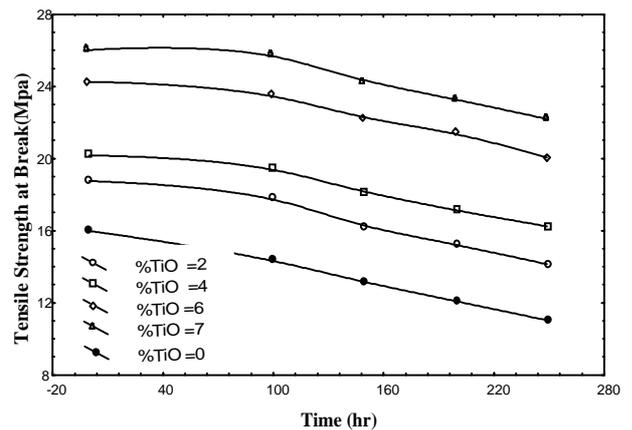
**Figure 4 Tensile strength at break of LDPE as a function
of exposure times at different wt.% of TiO₂ and
constant Fe₂O₃ content (7% wt) .**
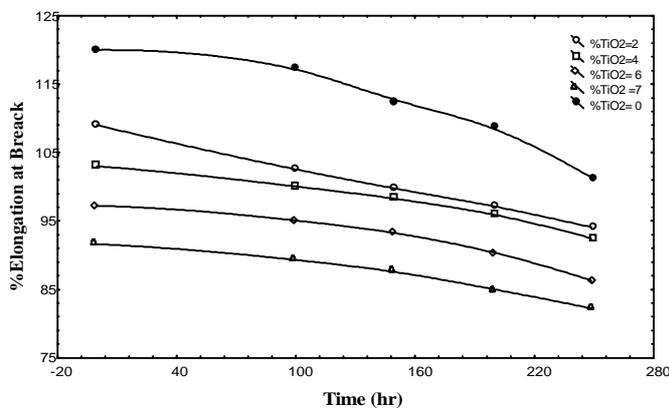
**Figure 5 %Elongation of LDPE as a function of
exposure times at different wt.% TiO₂and constant
Fe₂O₃ content**

**Figure 6 %Elongation of LDPE as a function of
exposure times at different wt.% Fe₂O₃and constant
TiO₂ content (7% wt).**

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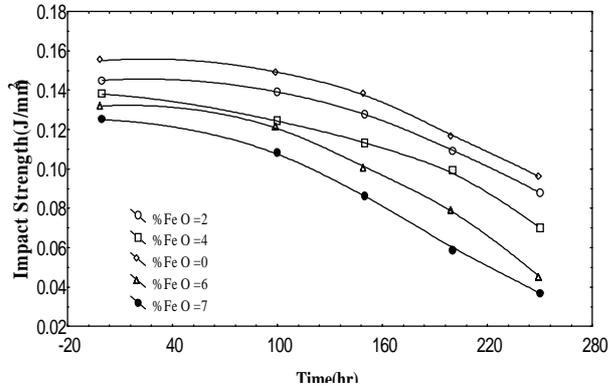
Figure 7 impact strength of LDPE as a function of exposure times at different wt.% TiO₂and constant

Figure. 8 impact strength of LDPE as a function of exposure times at different wt.% Fe₂O₃and constant
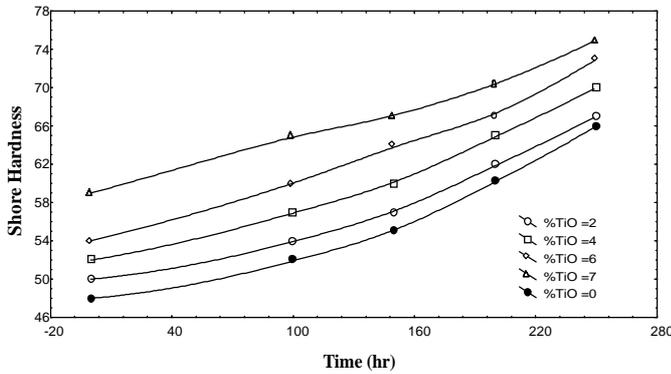

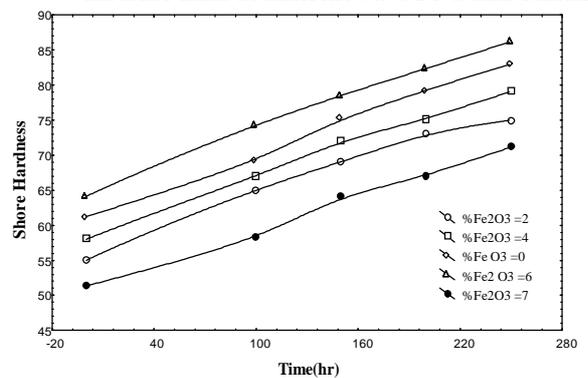**Figure 9 Shore Hardness of LDPE as a function of exposure times at different wt.% TiO₂and constant Fe₂O₃ content**

Figure. 10 Shore Hardness of LDPE as a function of exposure times at different wt.%Fe₂ O₃₂and constant TiO₂content
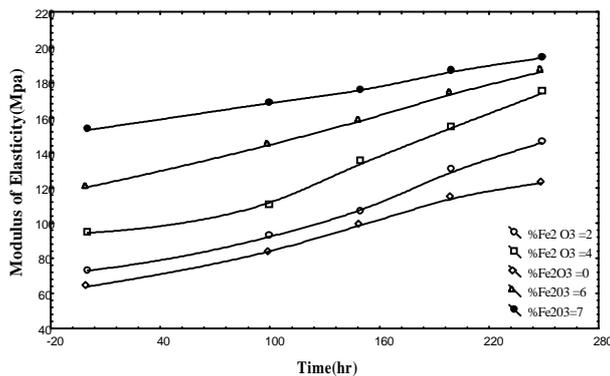
Figure. 11 %Modulus of elasticity of LDPE as a function of exposure times at different wt.% Fe₂O₃ TiO₂and constant TiO₂ content
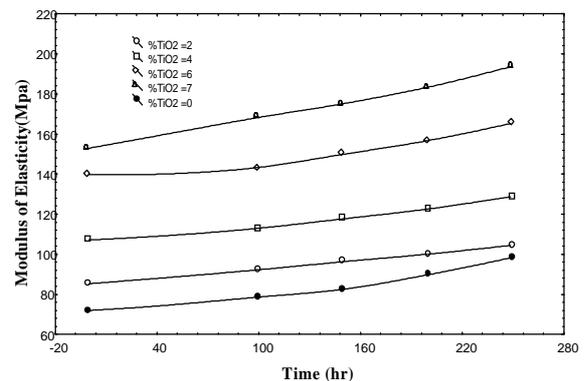

Figure 12 %Modulus of elasticity of LDPE as a function of exposure times at different wt.% TiO₂and constant Fe₂O₃ content
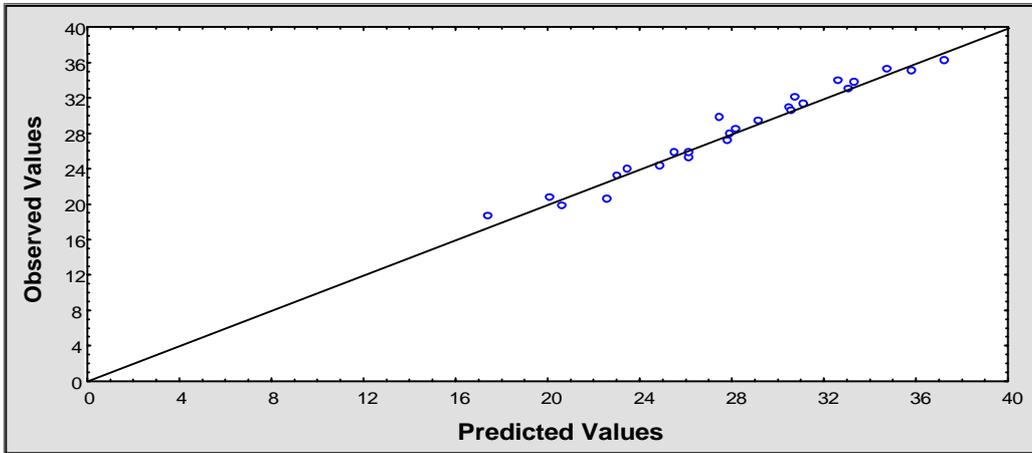
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Figure (13) Experimental versus predicted values for Eq.(1)
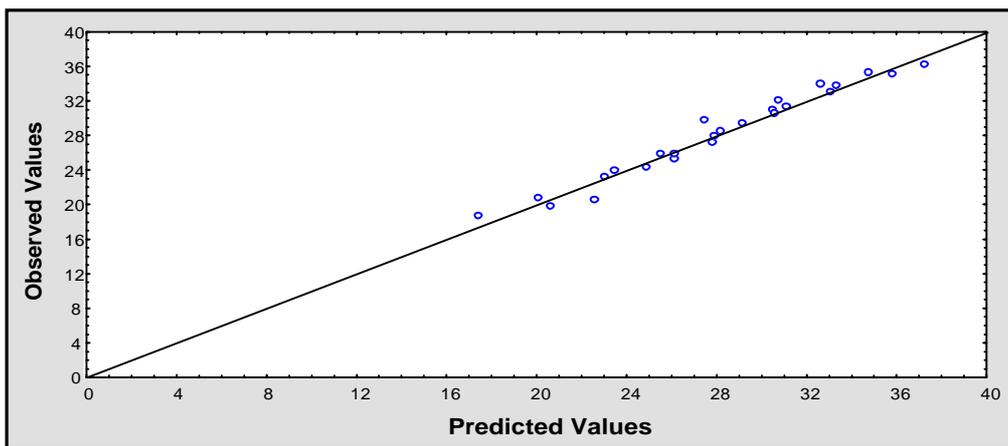
Figure .(14) Experimental versus predicted values for Eq. (2)

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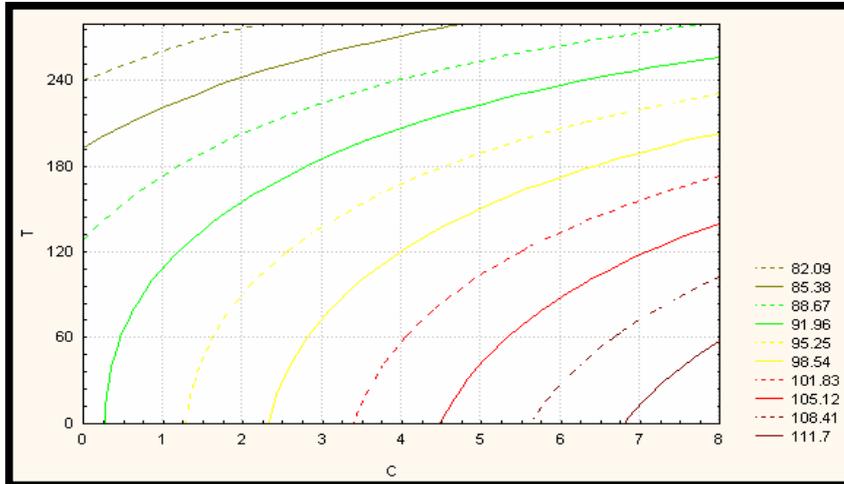and unpigmented LDPE

Figure (15)Contour plot obtained from (Exposure times,wt% of Fe$_2$O$_3$, modulus of elasticity).
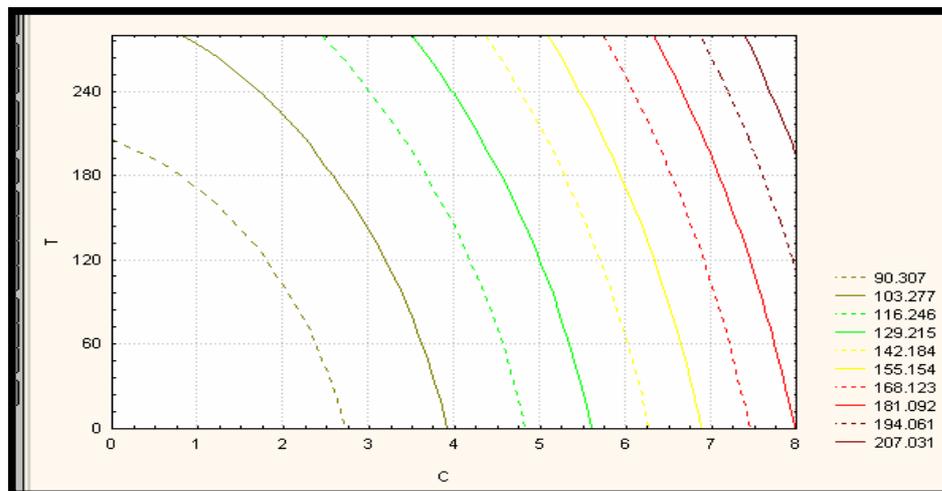

Figure (16) Contour plot obtained from (Exposure times,wt% of TiO$_2$, modulus of elasticity

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