The Diffusion Coefficients of Different Types of Liquid Environments Into Binary Polymer Blend

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Abstract

In this study, unsaturated polyester resin (UPE) and Natural rubber (NR) were used to prepared binary polymer blend (UPE/ NR) with weight ratio (95/5) %. The present paper investigates the diffusion behavior of three environmental groups , the first group is different types of water included (distilled water, tap water, rain water), the second is diluted solutions with same concentration (HCl , H_2SO_4, NaCl) and the third is solvents (ethanol, kerosene, benzene) and study their effects through (UPE/NR) polymer blend. Consequently, a set of specimens were immersed in various types of water, solutions and solvents for different periods of time. The diffusion coefficients (Dx) of these liquids were calculated based on Fick's law. The results of a series of experimental investigations showed that the values of (Dx) of all liquids are in the range (3.95- 9.1 $*10^{-12}$ m^2/s) except benzene which behaves another behavior called (non- Fickian diffusion) through the same time of immersion.

Keywords: polymer blends, Unsaturated polyester resin, Natural rubber, diffusion coefficient.

Introduction

Alloys and blends are simple mixtures of two or more plastics; there are no chemical or molecular links between the various polymer molecules [1].

There are many reasons why polymer blending is one of the most important areas in polymer research and development. Among these reasons, the most important is perhaps that polymer blends offer a fast and cheap way to obtain new polymeric materials. These materials generally exhibit a range of properties varies between the properties of their components. Moreover, their properties may be complementary and difficult to be found together in the case of a single component [2].

A related system of strengthening that came into use in the mid-1980s is the interpenetrating network (IPN): A cross – linked polymer is penetrated throughout with another polymer such that the penetrate becomes the matrix and the network polymer is like a three-dimensional reinforcement of the matrix polymer, or cross-linked polymers can have another polymer cross-linked within the network of the first polymer. A semi-interpenetrating network is compared with a fully interpenetrating network in Fig.(1). Semi IPNs are usually formed by polymerizing a linear polymer within the network of a cross-linked polymer; a fully interpenetrated network can be formed by cross-linking a second polymer within the network of a previously cross-linked polymer [1].

The chemical resistance of a polymeric material is its ability to withstand chemical attack with minimal change in appearance, dimensions, mechanical properties and weight over a period of time [3].

Yu and Selvadurai investigated the influence of ethanol exposure at different concentrations on the mechanical properties of a plasticized PVC membrane. Exposure to pure ethanol resulted in a reduction in flexibility, or embrittlement. The PVC membranes exposed to a mixture of ethanol and pure water in equal volume properties indicate that, after more than one year of exposure, the PVC membranes became softer greater deformation under the same external load. This phenomenon can be attributed to the swelling of the PVC membrane [4].

Seo *et al*. [5] prepared Epoxy/ Bismaleimide (BMI) composites. The thermal properties and water sorption behaviors of the epoxy and BMI composites were investigated. The diffusion coefficient and water uptake deceased and the activation energy for water diffusion increased with increasing BMI content, indicating that the water sorption in epoxy resin, which causes reliability problems

in electronic devices, can be diminished by BMI addition.

Katoch *et al*.[6] studied new system of saturated polyester and their nanocomposites synthesized from glycolyzed PET with varied composition. The sorption and diffusion studies in water were investigated. The diffusion coefficient of saturated polyester samples decreases with an increase in glycolyzed PET contents. The nanocomposite samples show less diffusion coefficient than pristine polymer and it decreases with an increase in nano-filler up to 4 wt%. The diffusion coefficient increases with an increase in temperature for all the samples.

Ramesh *et al*.[7] prepared silicone-polyester blended coatings for corrosion protection. The network of different functional groups between silicone and polyester resins was examined by FTIR spectroscopy. Electrochemical Impedance Spectroscopy (EIS) was used to study the anticorrosion property of the systems by exposing the samples to 3% NaCl solution. EIS experimental results show that the coatings could protect the metal surface for the exposure to corrosive medium for more than 30 days.

The objective of the present work is to study the diffusivity of some liquids into (UPE/NR) polymer blend for determining the diffusion coefficients (D_X) of them and investigate their effects on the external appearance nature and morphology of the blend.

Experimental Part

(UPE/NR) polymer blend with weight ratio (95/5)% was prepared by mixing Unsaturated polyester resin (UPE) with Natural rubber (NR). The polymers used in this work were commercial products.

(UPE) resin was supplied by (SIR) company, Saudi Arabia. After mixing the two previous polymers, the hardener of (UPE) was added to the mixture. The addition ratio of hardener(Methyl Ethyl Ketone Peroxide (MEKP)) is (2%) of resin. An acceleration material of reaction (cobalt octoate in dibutyl phthalate) was added with ratio (0.5%) of resin.

This binary polymer was poured in a metal mould with dimensions (14, 12, 3) cm^3 at room temperature, then after solidification, the resulted cast of blend was put in an oven with (Temp. = 50°C) for (1 hour) to ensure that a full cure was achieved. According to the standard specification (ASTM-D570), the samples were cut in cubic shapes from the polymer blend under study.

By using the grinding machine, the surfaces and edges of specimens were smoothed for minimizing surface defects and obtaining the uniform samples.

The initial masses of prepared specimens were obtained by using sensitive electronic balance type (Mettler, model AE160) with 0.0001g resolution.

The samples were subjected for different types of liquids included [(distilled water, tap water, rain water), (HCl, H$_2$SO$_4$, NaCl), (ethanol, kerosene, benzene)] at room temperature. The dry samples were immersed into sealed containers that contain (150ml) for each type of water and solutions that mentioned above.

Weight changes were monitored by repeated weighting of the samples. The percent weight change during immersion was calculated using the following equation:-

$$Wt.(\%)(t) = \frac{w(t) - w(0)}{w(0)} \times 100 \quad ....(1)\ [8,9]$$

Where Wt.(%) is the percent weight change at time (t), w(t) is the weight of the tested specimen at time (t), and w(0) is the dry specimen weight.

The diffusion coefficient (Dx) can be calculated from the initial slope (m_x) of the absorption curve in region (I) using the equation:-

$$Dx = \pi\ [m_x\ d\ /4\ M\infty\ ]^2 ....(2)\ [8,9]$$

Where M∞ is the equilibrium moisture content when the slope of the curve converts to straight line as shown in Fig.(2).
d is the initial thickness of the specimen.

The output from a diffusion experiments at a given temperature is the percent weight gain versus square root of time, √time.

Optical microscope (15X) type (73346/digital camera, Japan) was used to study the morphology and microstructure of specimens after the immersion in these liquids.

Results and Discussion

The kinematics of water penetration in polymers varies with the nature of system that is being considered and the exposure conditions. In the simplest case, water or solution enter the polymer without interacting with the molecular segment network. This case can be represented by Fick's law, which assumes that the absorption is a diffusion process only driven by the moisture concentration gradient. Frequently, however, the Fickian model does not adequately represent the absorption process. Such cases are called non-Fickian, or anomalous diffusion [10].

The simplest moisture diffusion model in this case is based on Fick's law, which is represented mathematically by:

$$\partial c / \partial t = D \ (\partial^2 C / \partial x^2) \ \dots\dots\dots\dots\dots\dots\dots(3)[9]$$

Where c is the moisture concentration, t is the time, x is the spatial coordinate, and D is the diffusivity.

Table (1) lists the values of diffusion coefficients of liquids through the polymer blend under work at room temperature. The diffusion coefficients of the different types of water (distilled, tap, rain) into (UPE/NR) polymer blend are in the range $(8-9)*10^{-12}$ m^2/s, which are close to the results obtained by other investigators.

From the definition of interpentrating polymer networks that mentioned in the introduction, it can be concluded that the prepared polymer blend (UPE/NR) is seminterpetrating polymer network (Semi IPNs) as shown in Fig.(2). Unsatorted polyester resin is cross-linked polymer while the Natural Rubber is linear polymer [1, 2].

Fig.(3-6) represent optical micrographs of all prepared specimens before and after the immersion. From these Figures, it can be seen that there is some voids, swelling and cracks after all the cases of immersion especially with HCl, NaCl and ethanol. These defects may be related to penetrate these solutions within the structure of polymer blend more than other liquids under work. It can be also seen observable change in the nature and colour (changed to dark) of the polymer blend that immersed into benzene as shown in Fig.(5c).

Figs.(7-15) present the percent weight change of samples as a function of the square root of immersion time into different types of liquids under study. The solid line in the same figures shows the sigmoidal fitting for the experiments data assuming Fickian diffusion [8,11,12]. The absorption curves display a pronounced linear region extending up to about 60% of the total absorption range and then are concave to the abscissa above the linear portion, these results agree with previous studies [13]. The results show a Fickian behavior up to approximately 70 days of all specimens (except the sample immersed into benzene). It can be concluded that the (UPE/NR) polymer blend has good chemical resistance towards the corrosive solutions.

From Fig.(15), it can be seen that the saturation case is not obtained after the immersion into benzene solvent comparing with other liquids at the same time of immersion.

Conclusions

After carrying out the current study, it can be concluded that there is some changes in the colour of the prepared polymer blend after the immersion into kerosene and benzene for (70) days. It is clear that the changes associated with immersion were due to the plasticization case of material specimens rather than hydrolysis. The diffusion behavior of benzene through the polymer blend is different comparing with other liquids under study at the same time of immersion so that it can be say that (UPE/NR) polymer blend has chemical resistance towards these environments (except benzene) at this time of immersion.

Table (1)
Values of the diffusions coefficients (Dx) of liquids into polymer blends
(UPE/NR) at room temperature.

Immersion type	Dx $*10^{-12}$ m^2/s	M∞ (%)
Distilled water	9.098	1.326
Tap water (pH=7.1)	8.07	1.46
Rain water (pH=7.7)	8.88	1.491
HCl (0.25N)	8.607	1.358
H_2SO_4 (0.25N)	3.955	1.109
NaCl (0.25N)	8.442	0.901
Ethanol	7.115	1.39
kerosene	6.444	1.084
benzene	*	*

*** The behavior is different after the immersion in benzene, there is no saturation, and the mechanism of diffusion is anomalous when it is compared with other liquids.**
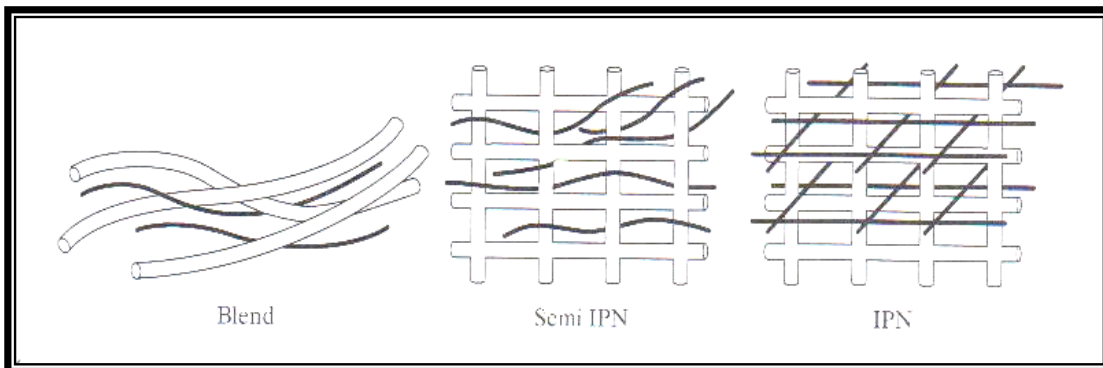
Fig.(1) Formation of interpenetrating networks formed by interpenetrating cross-linking of different polymers [1].
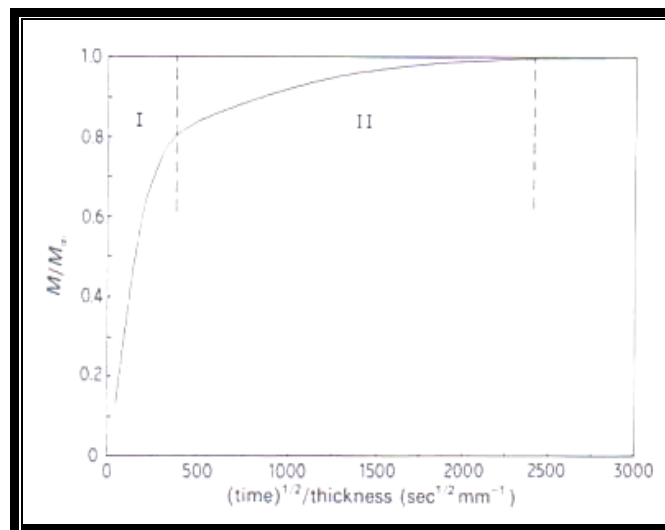
Fig.(2) Schematic absorption curve for a two phase resin system showing absorption into both the dense and less dense phases (region I) and the dense phase alone (region II)[11].

Fig.(3) Optical micrograph of (UPE/NR) polymer blend before immersion(15X).
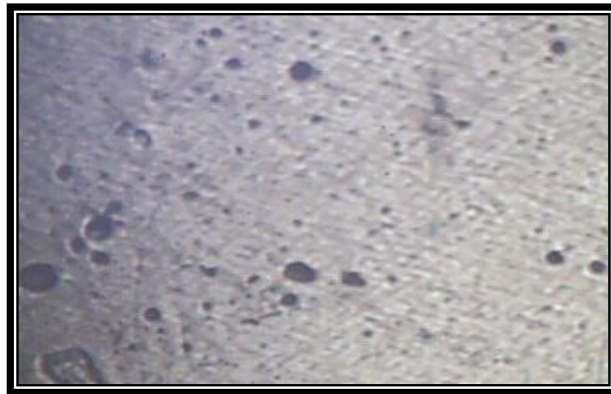
(a)

(b)

(c)

Fig.(4) Optical micrograph of (UPE/NR) polymer blend after immersion into
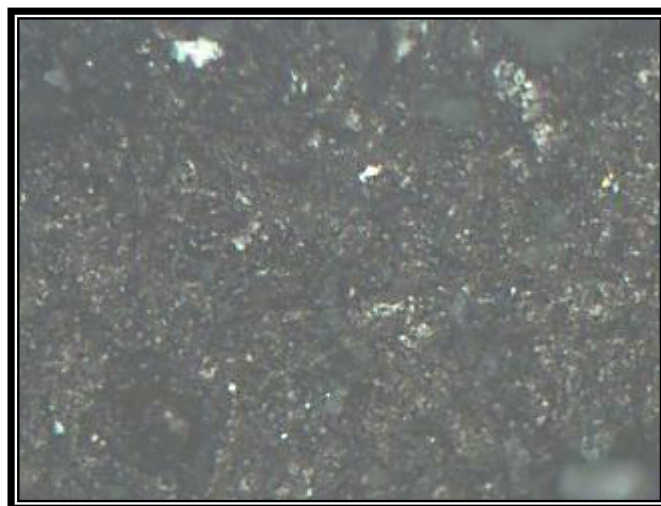*(a) distilled water, (b) tap water, and (c) rain water(15X).*

(a)

(b)
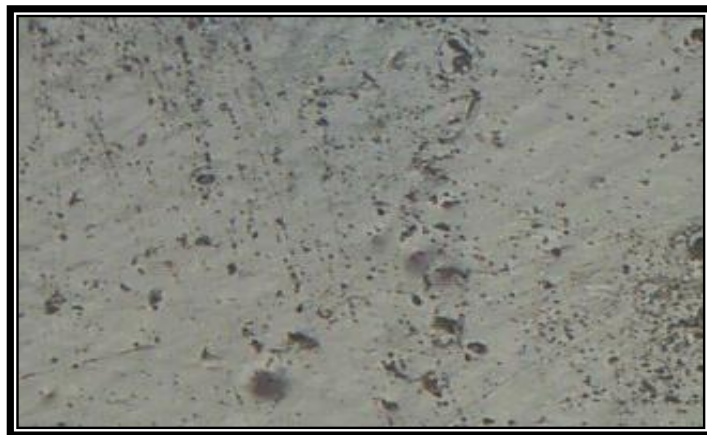
(c)

Fig.(5) Optical micrograph of (UPE/NR) polymer blend after immersion into (a) HCl, (b) H₂SO₄, and (c) NaCl (15X).

(a)
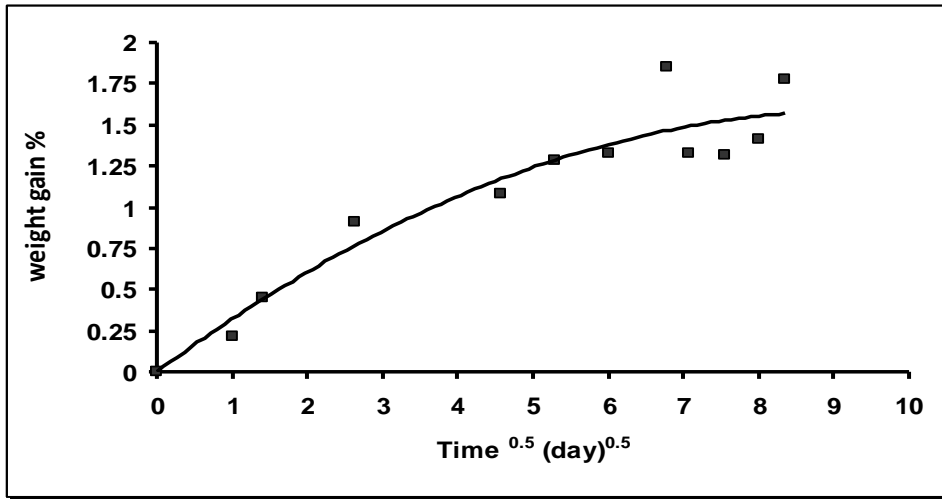

(b)

(C)

Fig.(6) Optical micrograph of (UPE/NR) polymer blend after immersion into (a) ethanol, (b) kerosene, and (c) benzene (15X).
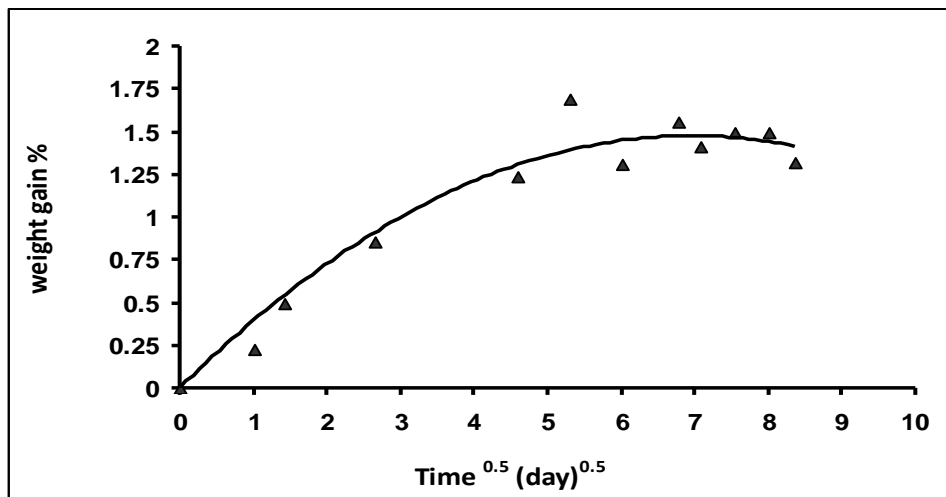
Fig.(7) Weight gain% of (UPE/NR) polymer blend with square root of immersion time in distilled water.
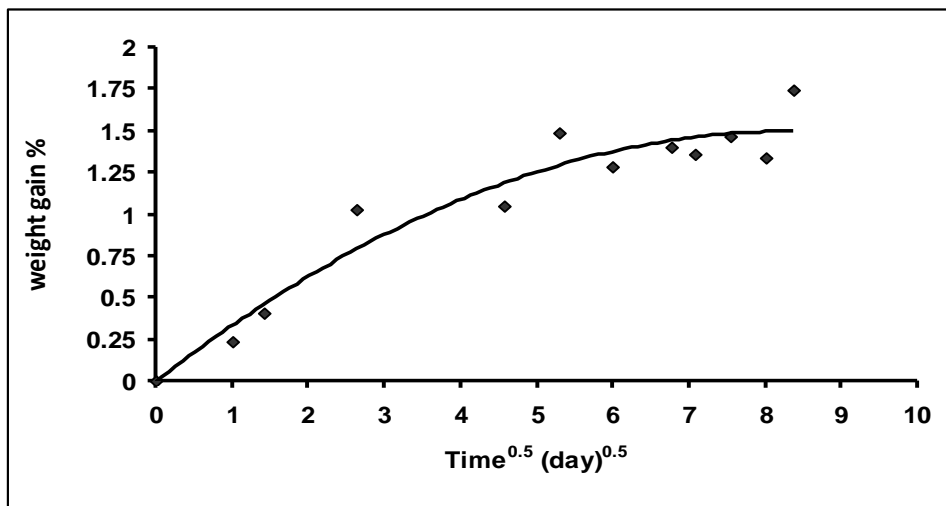
Fig.(8) Weight gain% of (UPE/NR) polymer blend with square root of immersion time in tap water.

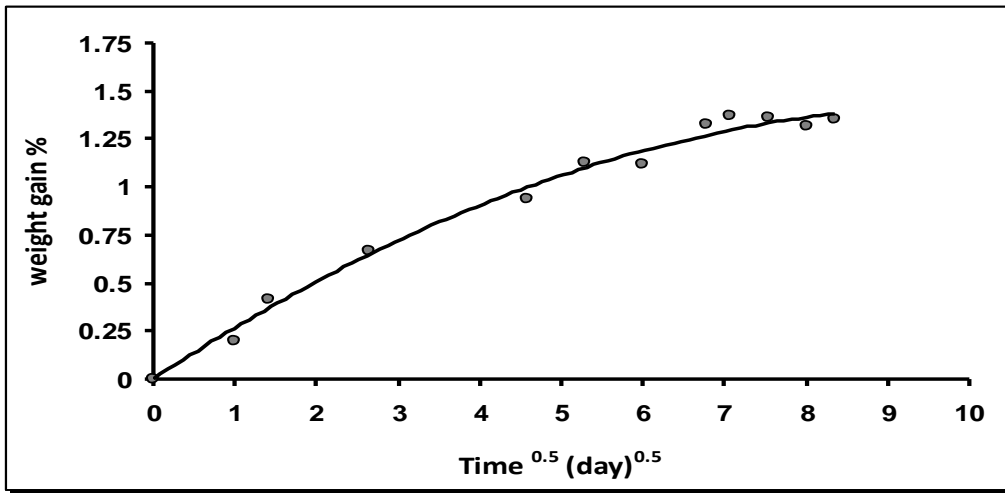*Fig.(9) Weight gain% of (UPE/NR) polymer blend with square root of immersion time in rain water.*

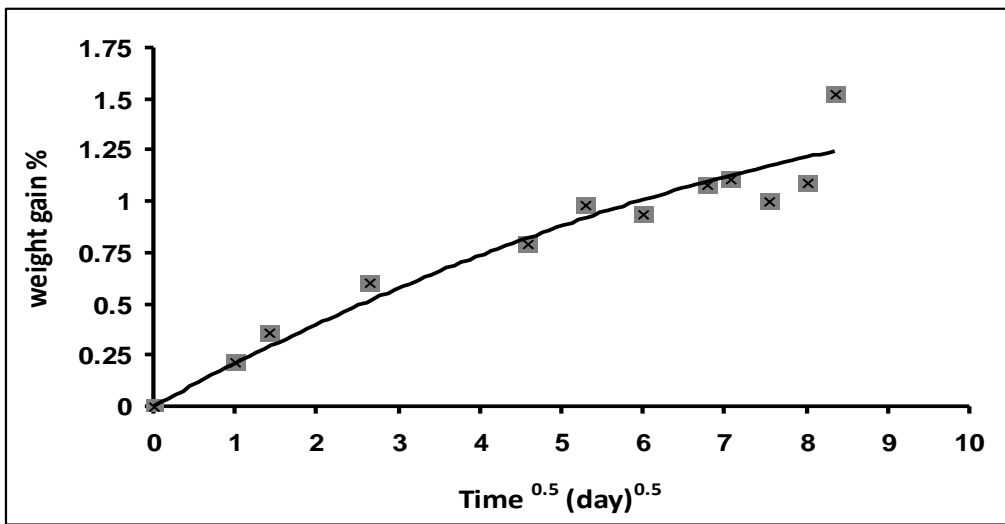*Fig.(10) Weight gain% of (UPE/NR) polymer blend with square root of immersion time in HCl acid.*

Fig.(11) Weight gain% of (UPE/NR) polymer blend with square root of immersion time in H_2SO_4 acid.
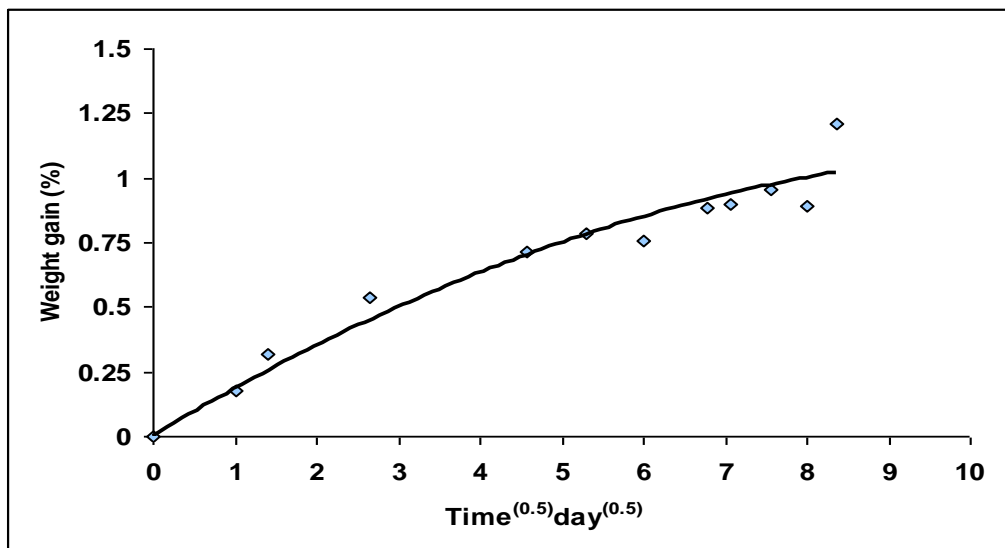

Fig.(12) Weight gain% of (UPE/NR) polymer blend with square root of immersion time in NaCl salt.
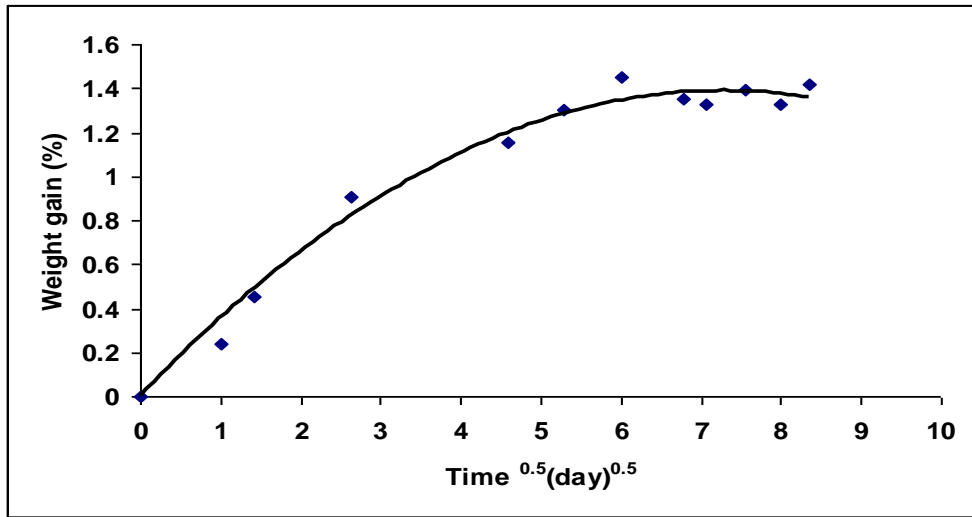
Fig.(13) Weight gain% of (UPE/NR) polymer blend with square root of immersion time in ethanol .
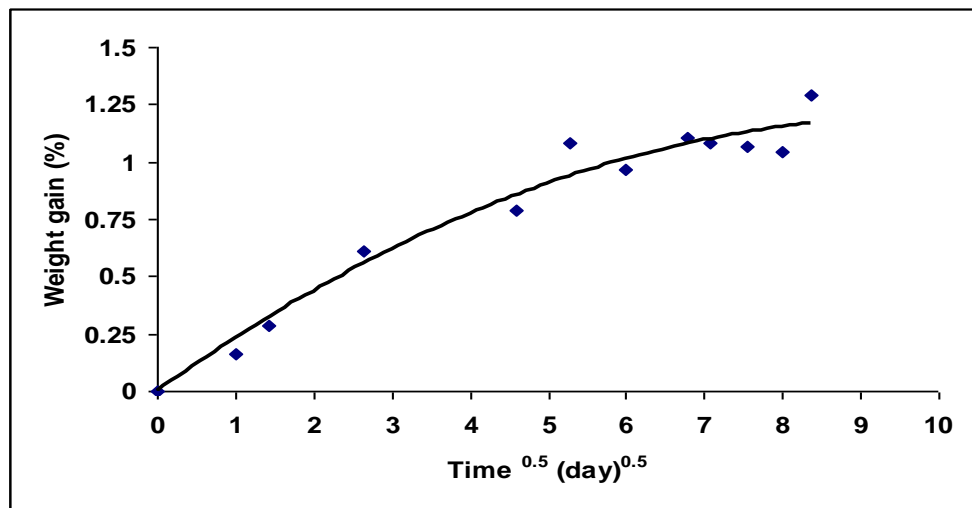

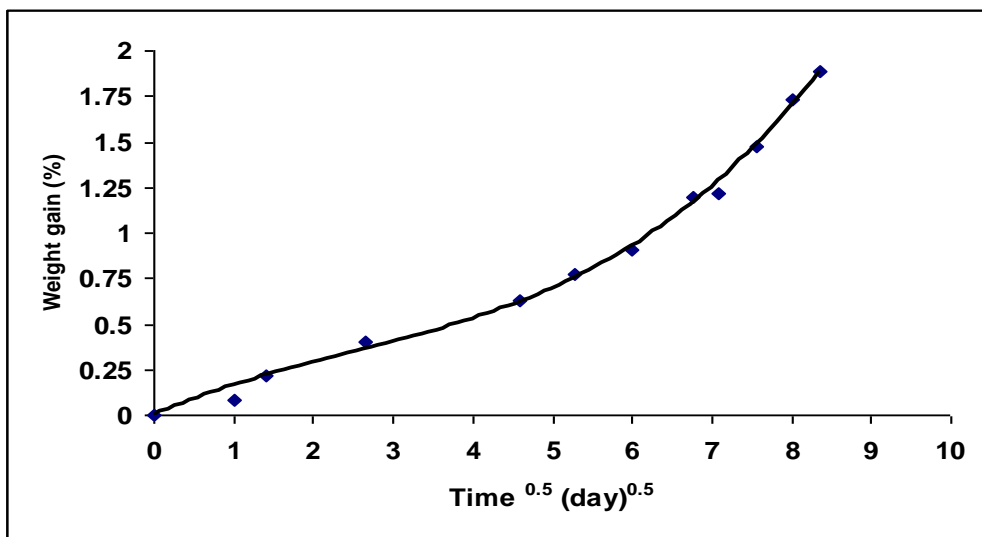*Fig.(14) Weight gain% of (UPE/NR) polymer blend with square root of immersion time in kerosene.*

Fig.(15) Weight gain% of (UPE/NR) polymer blend with square root of immersion time in Benzene .

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الخلاصة

في هذا البحث، أستخدم راتنج البولي استر غير المشبع (UPE) والمطـاط الطبيعـي (NR) لتحضـير خلـيط بـوليمري ثنائي (UPE/ NR) وبنسبة وزنية (95/5) %.

الدراسة الحالية تبحث السلوك الانتشاري لثلاثة مجاميع بيئية ، المجموعة الاولى هي انواع مختلفة من المياه شملت (الماء المقطر، ماء الحنفية، ماء المطر) والثانية هي محاليل مخففة وبنفس التركيز (HCl , H$_2$SO$_4$, NaCl) والثالثة هي مذيبات (الايثانول، النفط، البنزين) ودراسة تاثيراتها خلال الخليط البوليمري (UPE/NR). ولذلك غمرت مجموعة من النماذج في الانواع المختلفة من المياه والمحاليل والمذيبات لفترات زمنية مختلفة. معاملات الانتشار (Dx) لتلك السوائل تم حسابها على اساس قانون فك. اظهرت النتائج لسلسلة من البحوث التجريبية بأن قيم معاملات الانتشار (Dx) لجميع السوائل في المدى (3.95-9.1*10^{-12})m^2/s. ماعدا البنزين الذي يسلك سلوكا مغايرا حيث لايتبع سلوك فك في الانتشار خلال نفس الفترة من الغمر ويصطلح عليه (non- Fickian diffusion).