Study of Weathering Effect, and the Solution on the Diffusion Coefficient of the PET, Mineral Water, and Al-Badawi Vinegar Bottles samples

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Abstract

The aim of this work is to study the absorptive properties of PET, and bottle material samples for mineral water and black and white Al-Badawi vinegar (acidic acid (CH_3COOH)). PET samples were prepared by extrusion method, and take the bottle samples from the bottles, which are used as a container to save it. The fundamental reason for the permeability of polymers is their relatively high level of molecular motion. Since two different solutions were used to evaluate the diffusion behavior of specimens. By using mineral water for two kinds of specimen (PET, and samples of the bottle material at three conditions ((1)-indoor,(2)- in refrigerator, and(3)-outdoor) to study the weathering effect on polymer absorptive involved. It was found that PET-3(out door) was the most water absorbing polymer. It was attributed to free radical induced by the photo degradation, and the PET-2, and bottle samples (2-in refrigerator) were the lowest, which attributed to the thermal and photo degradation for the out door condition, whereas the lowest for the samples(2-in refrigerator). It was attributed to the freezing free radical in polymer of the lowest effect, so the weight gain will be the lowest. The diffusion coefficient of the bottle samples (2-in refrigerator) was of the lowest value (previous reasons), and also attributed to the bottle sample material (PET+ Additives (as stabilizers)), which caused in decreasing in thermal, and photo degradation effects.By using acidic acid at different concentration (4.6%, 6.4, and 100% of CH_3COOH)) as black, and white Al-badawi vinegar, and pure acidic acid. It was found increasing in absorptive with increasing of CH3COOH concentration, so the best absorptive for the highest concentration (100%) for two samples (PET, and bottle samples). CH_3COOH had a deterioration effect. This effect had led to formation of voids and gaps, beside the ones originated in the specimens during manufacturing and processing stages, and these gaps would be filled with the solutions, leading to an increase in weight. It was concluded that the diffusion coefficient was very low for all samples and in all solutions of order less than $10^{-14}m^2/sec$, so it was recommended to use PET for manufacturing the bottle(container) to save the solutions(water, and acidic solution, because it was a good barrier for solutions.

Keywords: absorptive, PET, acidic acid ,coefficient diffusion

Introduction

Polyethylene terephthalate (aka, PETE or the obsolete PETP or PET-P) synthetic fiber, beverage,are used food and liquid containers and engineering resins often in combination with glass fibers. It is one of the important raw materials, used in man-made fibers, depending on its processing and thermal history.

It may exist both as an amorphous (transparent) and as a semi-crystalline (opaque and white) material. PET can be semi-rigid to rigid [1], depending on its thickness, and is very lightweight. It makes a good gas and fair moisture barrier, as well as its impact strength.

PET bottles are excellent barrier materials and are widely used for soft drinks. PET is also used as a thermal insulation layer on the outside of the international space station [2].
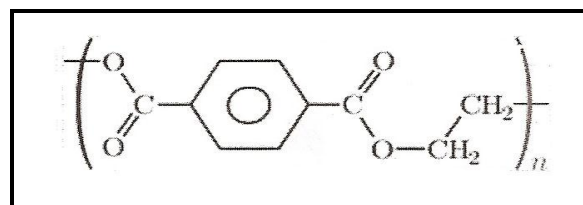

Fig. (1) Chemical structure of PET [2].

Polymers, unlike metals and ceramics, have the ability to absorb water or solutions. This should be taken into account when manufacturing polymeric containers and pipes. Absorptivity is affected by factors like solution itself, temperature, and time of exposure to the solution [3].

Many studies have been done to investigate decomposition by chemical factors and their effects on polymers. Hydrolysis is one of these effects, where some polymer interactions occur due to prolonged exposure to environment [4].Absorption usually follows Fick's law(*Quantity of water absorbed increases directly with square root of time. Then decreases gradually until a steady state is reached*) [5].

Diffusion can be defined as the process by which matter moves from one position to another in the system because of random molecular motion. Diffusion occurs in all fluids, since their atoms are moving continuously, so these atoms change their positions continuously. This behavior is described by Fick's first law of diffusion, which states that flux is proportional to concentration gradient (dc/dx):

$F_x = -D \, dc/dx$ ....(1)

Where:

F_x = Number of diffused atoms towards concentration C per second per unit area (Flux of molecules)

D= diffusion coefficient.

Fick's first law of diffusion is applied to constant concentration i.e. concentration does not change with time [5].

A material can absorb humidity and solutions in three stages [5]:

▪ Stage 1: includes the natural mechanism of diffusion and permeability.
▪ Stage 2: states the change in specimen's dimensions occurring due to permeability (Hydro elasticity), i.e. material swelling with 5
▪ Stage 3: deterioration and degradation of properties due to attack of moisture and solutions.

Certain types of radiations (electron beams, x-rays, β- and γ-particles, and ultra violet radiation) possess sufficient energy to penetrate a polymer and interact with the constituent atoms or their electrons. One of such reactions is ionization, in which the radiation removes an orbital electron from a specific atom, converting it into a positively charged ion.

Consequently, one of the covalent bonds associated with a specific atom is broken and a rearrangement of atoms occurs at that point.

This bond breakage leads to either scission or cross-linking at the ionization site, depending on the chemical structure of the polymer and the dose of radiation [6].

Polymers are susceptible to weather factors (U.V. radiation, humidity, and temperature) because they are used in a wide range of outdoor applications.

Ultra violet radiation is one of the harmful weather effects on polymers. Although a small percentage of U.V. reaches earth surface (about 3% of spectrum), it has sufficient energy to break the bonds of polymer chains, since these bonds have specific energy to break and this energy lies in the range of U.V. spectrum (200-340)nm. And the most effective wavelengths that affect polymers lie in the range (290-315)nm, which is called U.V.-B[7]. When polymers are exposed to radiation, they will reveal some changes, like [8]:

1- Embrittlement of material, leading to cracking,
2- Flaking of the surface with pitting,
3- Color changes and chalking,
4- Blistering of surface layers,
5- Changes in mechanical and electrical properties.

Cross linking in polymers will turn them from being flexible to brittle materials , also the chain scission will change polymers from solid, strong polymers to a waxy state. Another effect in degradation process is the presence of oxygen that reacts with irradiated polymer to form peroxide and then hydro peroxide [9].

Experimental Part

PET, and water and Albadaway-Vinegar bottles are the material used and procedure of work are discussed, with illustration of the tests carried out on specimens.

Most thermoplastic pellets are highly hydrophilic; they absorb a considerable percentage of moisture from the environment. Hence, they are dried in an oven, each type in a separate batch, at different temperatures.

Polyethylene terephthalate was dried, using the oven, and then the dried batches were wrapped in aluminum foil with sacks containing silica gel, to avoid the adsorption of moisture as much as possible, and were stored to be used in extrusion.

In order to prepare the extrusion batch, the pellets were weighed according to the ratios mentioned previously. The electronic scale (Mettler AE 200) was used in this process. Each batch weighed 300 gm.

The extrusion process was carried out in a single screw extruder, in which the batch of pellets is fed through a hopper to the barrel, which is heated to the desired temperatures to melt the components and the melt gets out at the other end of the barrel. The temperatures of the barrel were set as two heating zones, the first heating zone is near the hopper, and is heated to a temperature that is lower than the melting point of the polymer, to preheat it and facilitate its melting, at the second zone, near the outlet of the barrel, at which the full melting takes place, the temperature at this zone is set higher than the first zone.

The temperatures of the two zones were set as [(220 and 260) °C in the first and second zone respectively, for polyethylene terephthalate.

The screw, which rotates at a speed of 36 rpm, pushes the melted polymers through the heated barrel while mixing the pellets, the melt passes through a die to gain the flat shape, the die is of rectangular shape, which gives a tape shaped product which passes through rotating rolls to flatten its surface and finally the product is immersed in cold water tub for cooling.

The tape is cut into samples needed for inspection and test, according to the specification of each test. The thickness of the tape product ranges between (0.5-1) mm.
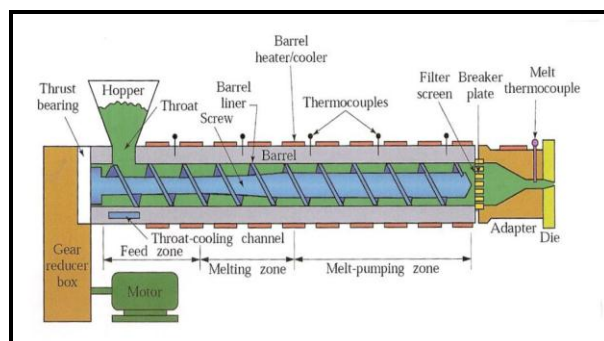

Fig. (2) The internal structure of the extruder [10].

The used samples are listed in Table (1):

Table (1)
The used samples in research.

Prepared samples	Definition	Case	Solution
PET-1	PET prepared by extrusion method	indoor	Water
PET-2	PET prepared by extrusion method	outdoor	Water
PET-3	PET prepared by extrusion method	In-refrigerator	Water
Samples-1	Specimen took from mineral water bottle	indoor	Water
Samples-2	Specimen took from mineral water bottle	outdoor	Water
Samples-3	Specimen took from mineral water bottle	In-refrigerator	Water
PET-4.6%	PET prepared by extrusion method	/	4.6% CH_3COOH Concentration.
PET-6.4%	PET prepared by extrusion method	/	6.4% CH_3COOH Concentration.
PET-100%	PET prepared by extrusion method	/	100% CH_3COOH Concentration.
Samples-4.6%	Specimen took from mineral water bottle	/	4.6% CH_3COOH Concentration.
Samples-6.4%	Specimen took from mineral water bottle	/	6.4% CH_3COOH Concentration.
Samples-100%	Specimen took from mineral water bottle	/	100% CH_3COOH Concentration.

The mass of the samples was weighed before immersion using a four digit sensitive electronic balance (Mettler AE 160), then, these samples, and water and Albadaway – Vinegor bottles samples were immersed in two solutions:

a) mineral water , and left the bottle out the door,in door, and in refrigerator.

b) albadaway-Vinegar (whit and black) in to concentrations (4.6% for black vinegar, and 6.4% white khall, and 100% CH_3COOH. After (3) days, the samples were taken out using tweezers.

The samples were weighed after being dried. This process was repeated every 3 dayes for 2 months.

The percentage of the change in mass for the samples placed in the solutions was calculated as follows [11]:

$$\text{Weight gain} = \frac{M_2 - M_1}{M_1} \times 100\% \quad ....(2)$$

Where

M_1: mass of the sample before immersion in (gm)

M_2: mass of the sample after immersion in (gm).

The curves of the absorption percentage with the square root of time were plotted for all prepared samples.

Diffusion coefficient (D) was calculated by applying the following equation [12]:

$$D = \pi \left[\frac{kb}{4M\infty} \right]^2 \quad ....(3)$$

Where

K is the slope of straight line of the curves, which represents the relation between the weight gain % and √time.

b: sample thickness (mm),

$M\infty$:optimum weight gain [max weight absorbed] (gm).

Results and Discussion

The study of transport of liquids through polymers is important for a variety of engineering applications. The transport of liquids cases polymers to swell and the extent of swelling depend on temperature, chemical nature, and the degree of cross linking of polymer in addition to the molar mass of polymer and of liquid molecules.

The diffusion of polymer members is classified into three types. In the first case, the rate of diffusion can be much smaller than that of polymer relaxation due to physical changes in polymer-solvent system. Such types of systems are said to be Fickian or Case I. In case II or non-Fickian type diffusion, the rate of diffusion is much greater than of polymer relaxation. In the anomalous type of diffusion, both the rate of diffusion rate and the relaxation rate are nearly the same.

As swelling increases, free volume increases due to increased chain mobility, which facilitates transport process [13].

The solute diffuses into and is absorbed within the polymer: the small solute molecules fit into and occupy position among the polymer molecules. Thus the macromolecules are forced apart such that the specimen expands or swell. Furthermore, this increase in chain separation results in reduction of the secondary intermolecular forces [14].

The fundamental reason for the permeability of polymers is their relatively high level of molecular motion [15]. Since two different solutions were used to evaluate the diffusion behavior of specimens. By using mineral water for two kinds of specimen (PET, and samples of the bottle material at three conditions ((1)-indoor, (2) - in refrigerator, and (3)-outdoor)
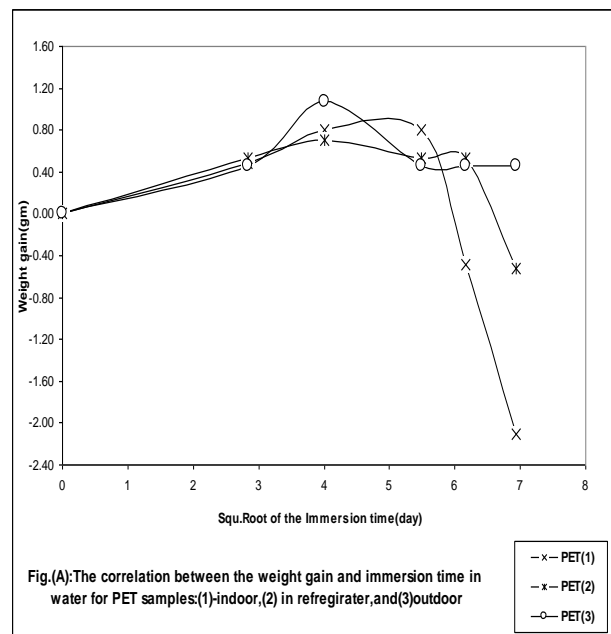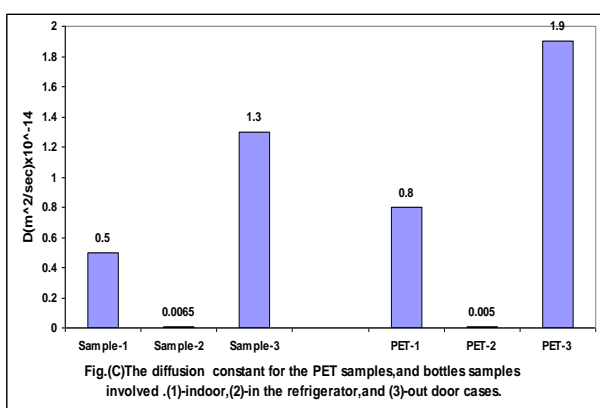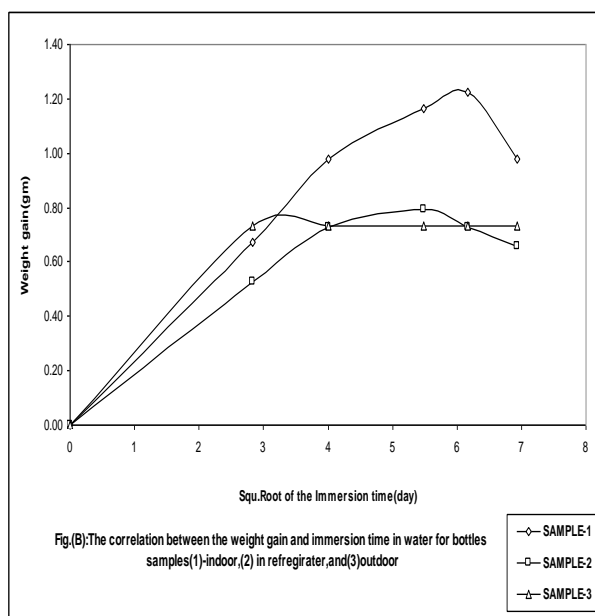

Fig.(A):The correlation between the weight gain and immersion time in water for PET samples:(1)-indoor,(2) in refregirater,and(3)outdoor

Fig.(B):The correlation between the weight gain and immersion time in water for bottles samples(1)-indoor,(2) in refregirater,and(3)outdoor

◇ SAMPLE-1
□ SAMPLE-2
△ SAMPLE-3

Fig.(C)The diffusion constant for the PET samples,and bottles samples involved .(1)-indoor,(2)-in the refrigerator,and (3)-out door cases.

First PET-3(out door) was the most absorbing polymer, and this is true in mineral water, as shown in Fig. (1). this explains the weight gain that occurred first. Thus the liquid absorbance began to cause polymer deterioration leading to weight loss, which was gradual over a period of 6 days, until a steady state is reached, leading to a stable weight of the specimens. This behavior was different than the other condition –indoor, and –in-2-the refrigerator, which was attributed to photo degradation. Photo degradation induced new interfaces that were susceptible to chemical attack that took place at these relatively weak points [16].

The liquid transformation process causes polymer swelling .The increasing in swelling depends on temperature, material type, and the cross linking degree. Increasing in swelling causes increasing in free volume induced by increasing in chain mobility, which simplified the transformation process, and

the diffusion of solution into the polymer (absorption of the solution into the polymer). The molecules of the solution equips the sites between the polymer molecules caused in polymer extension, and swelling, which induced in decreasing in binding forces of the molecules. The percentage of the absorptive was calculated for PET, and bottle samples by using the equation (3), at different conditions ((1)-indoor, (2) in refrigerator, and (3) outdoor) to study the weathering effect on polymer absorptive involved. Fig.(A), and Fig.(B) show the correlation between the weight gain and the square root of the immersion time in days. For the PET, and bottle samples (3-outdoor) were of highest weight gain, and the PET, and bottle samples (2-in refrigerator) were the lowest, which attributed to the thermal and photo degradation for the out door condition, whereas the lowest for the samples (2-in refrigerator), which attributed to the freezing free radical in polymer of the lowest effect, so the weight gain will be the lowest [13]. The diffusion coefficient of the bottle samples (2-in refrigerator) was of the lowest value (previous reasons) [16], and also attributed to the bottle sample material (PET Additives (as stabilizers)), which caused in decreasing in thermal, and photo degradation effects [15]. It was concluded: first that the diffusion coefficient for the (PET) was very low of 10^{-14} order, so it can be used to manufacture of water bottle, second: it was preferable to store the water bottle in the refrigerator Fig.(C).

Fig.(D):The correlation between the weight gain and squ.root of the immersion time

Fig.(E): The correlation between the weight gain and squ.root of the immersion time

Fig.(F)The diffusion constant for the PET samples,and bottles samples involved,for the 4.6%,6.4%and 100% CH3COOHconcentration cases
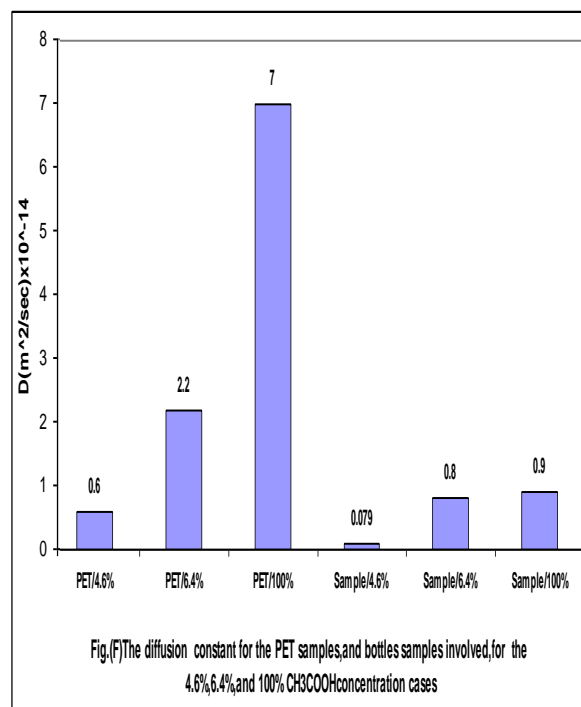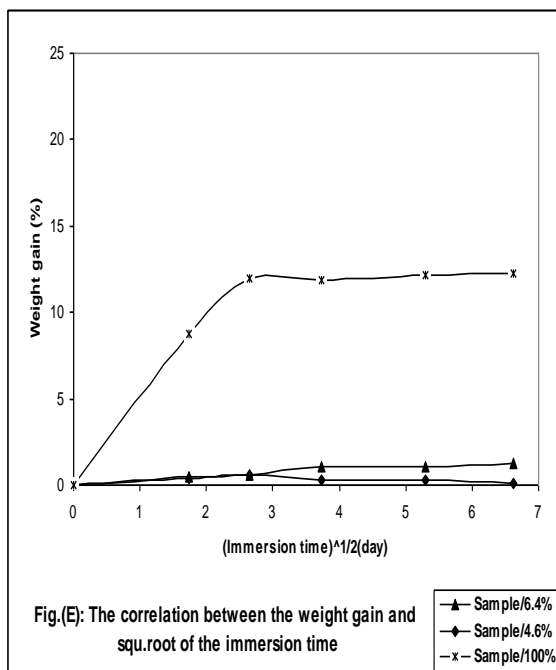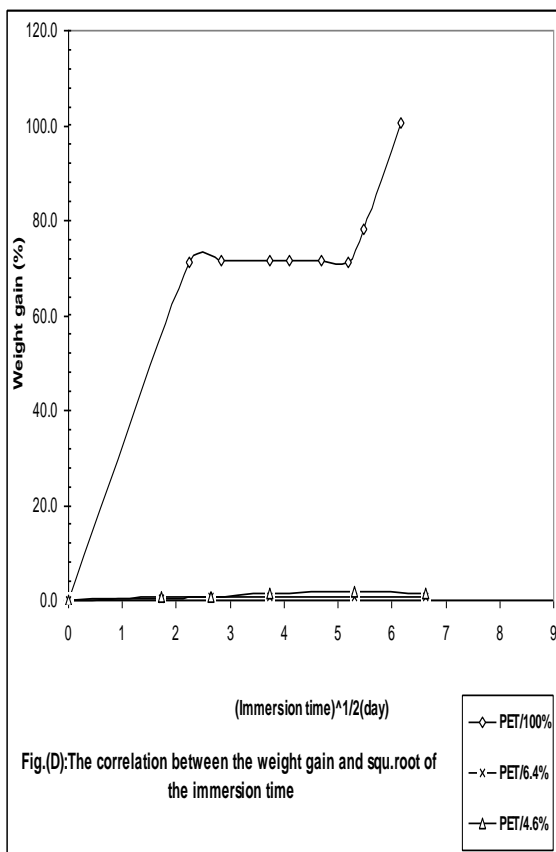
Fig.(4) Shows that 100%PET,and 100% bottle samples of highest absorptive, and decreases by acidic acid concentration decreasing.

Fig.(D), and Fig.(E) show increasing in absorptive with increasing of CH_3COOH concentration, so the best absorptive for the highest concentration(100%) for two samples (PET, and bottle samples).CH_3COOH had a deterioration effect, this effect had led to formation of voids and gaps, beside the ones originated in the specimens during manufacturing and processing stages, and these gaps would be filled with the solutions, leading to an increase in weight [16].

This may be explained as the voids and flaws existing on the surface and inside the specimens have been attacked and filled with solution, and this process occurred first, leading to swelling, the latter step separates polymers chains apart, the swollen polymer generates a sufficient pressure to destroy the intermolecular chains, leading to polymer degradation [16].

It is worth mentioning that the interfaces are prone to chemical attack, and this can be true for all samples in this study, and after attacking the interfaces, liquids will diffuse into material, resulting in more deterioration, Fig.(F) [3].

The results obtained agree with results obtained by other researchers, like Rula. A. [15]. In general the diffusion coefficient was

very low, so it was recommended to use PET for manufacturing the bottle(container) to store the solutions(water, and acidic solution), because it was a good barrier for solutions.

Conclusions

- By using mineral water for two kinds of specimen (PET, and samples of the bottle material at three conditions ((1)-indoor,(2)-in refrigerator, and (3)-outdoor) to study the weathering effect on polymer absorptive involved. It was found that PET-3(out door) was the most absorbing polymer. It was attributed to free radical induced by the photo degradationand, and the PET-2, and bottle samples (2-in refrigerator) were the lowest, which attributed to the thermal and photo degradation for the out door condition, whereas the lowest for the samples (2-in refrigerator). It was attributed to the freezing free radical in polymer of the lowest effect, so the weight gain will be the lowest. The diffusion coefficient of the bottle samples (2-in refrigerator) was of the lowest value (previous reasons), and also attributed to the bottle sample material (PET+ Additives (as stabilizers)), which caused in decreasing in thermal, and photo degradation effects. So it was recommended that we have to store the mineral water in the refrigerator, and taking into count the shipment condition.

- By using acidic acid at different concentration (4.6%,6.4, and 100% of CH_3COOH))as black ,and white Al-badawi Vinegar, and pure acidic acid. It was found increasing in absorptive with increasing of CH3COOH concentration, so the best absorptive for the highest concentration (100%) for two samples (PET, and bottle samples). CH_3COOH had a deterioration effect. This effect had led to formation of voids and gaps, beside the ones originated in the specimens during manufacturing and processing stages, and these gaps would be filled with the solutions, leading to an increase in weight. It was concluded that the diffusion coefficient was very low for all samples and in all solutions of order less than $10^{-14}m^2$/sec, so it was recommended to use PET for manufacturing the bottle (container) to save the solutions

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(PET،ومادة القنينة). يحدث الحامض CH_3COOH تلف في البوليمر.وان هذا التاثيريؤدي الى تكوين فجوات وفراغات، اضافة الى تلك التي تنشا خلال عملية تصنيع النموذج وعمليات المعالجة ،وان هذه الفجوات سيتم ملئها بالمحاليل ممــا يــؤدي الــى زيـادة فـي الوزن.نسـتنتج بـان معامـل الانتشارقليل جدا لجميع النماذج ولجميع المحاليل وهو من رتبة اقل من10^{-14}،لذا يوصى باستخدام PET في تصنيع القنـاني (الحاويـات) لحفظ المحاليل (المياه،والمحاليل الحامضية) كونها تعتبر حواجز جيدة للمحاليل.

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الخلاصة

ان الهـدف مـن هـذه البحـث هـو دراسـة خـواص الامتصاصية للبولي اثيلين ترفثاليت (PET) ونمـاذج من القناني التي تستخدم لحفظ المياه المعدنيةتوخل البدوي الابيض والاسود (حامض الخليكCH_3COOH).ان نمـاذج PET محضرة بطريقـة البثـق واخـذ نمـاذج مـن مـادة القنـاني،والتي تستخدم كحاويات لحفظها.ان السبب الرئيسي لامتصاصية البوليمرهو مستواها العـالي للحركـة الجزيئيـة.ونظرا لاستخدام محلــــــولين مختلفــــــين لتقيــــــيم سـلوك الامتصـاص فـي العينات.باسـتخدام الميـاه المعدنيـة (PET، ونماذج من القنينة وللحالات الثلاثة وضع العينات الغموره 1- داخل الغرفة،وضعها 2- في الثلاجة،واخيرا و ضعها 3- في الخارج) لدراسة تاثير التجوية على امتصاصية البوليمر مدار البحث.وجد بان (PET-3) ذي اعلى امتصاصية.يعزى ذلك الى الجذور الحرة المحثة بعمليـة التفكك الضوئي،وان نمـاذج (PET-2) والنمـاذج الماخوذة من القناني (الموضوعة2-في الثلاجة) ذوات ادنى امتصاصية.وقد اعزي ذلك الى الجذور الحرة المجمدة في البوليمر ذوات ادنى تاثير،لذا سيكون الربح في الوزن هو الاقل.ان PET معامل الانتشار لنماذج القناني الموضوعة في الثلاجة 2- ذوات اقل قيمة والمتسبب عن التناقص في تـاثير التفكك الحـراري والضوئي.باسـتخدام حـامض الخليـك بمختلف التراكيز (CH_3COOH 100% ,6.4%,4.6%) كخـل ابيـض واسـود وحـامض الخليـك المركز.وجـد بـان الامتصاصية تزداد بازديـاد تركيز CH_3COOH ،لذافان اعلى امتصاصية كانت لاعلى تركيز ولكلا النموذجين .