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Addition of Some Natural Pigments as Colorants and Stabilizers Materials for Polymers

A Thesis Submitted to the Department of Engineering Materials / College of Engineering-University of Babylon in a Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Engineering Materials

By

Zuhair Gabbar A١-Asadee

M.Sc. in Engineering Materials

Under supervision

Chief Res.	Assist Prof.
Dr. Jaleel K. Ahmed	Dr. Tahseen A. AL-Hattab

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٢٠٠٧ م- ١٤٢٨هـ

بِسۡمِ ٱللَّهِ ٱلرَّحۡمَٰنِ ٱلرَّحِيمِ

قالوا سبحانك لا علم لنا الا
ما علمتنا انك انت العليم
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Zuhair Gabbar Abdul-Ameir

Under our supervision at the Department of Engineering Materials /University of Babylon, as a partial fulfillment of the requirements to the degree of Doctor of Philosophy in Engineering Materials.

Signature:	Signature:
Name : Dr.Tahseen A. Al-Hattab	Name : Dr.Jaleel kareem Ahmed
University of Babylon	University of Babylon

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We, the examination committee certify that we have read this thesis entitled:

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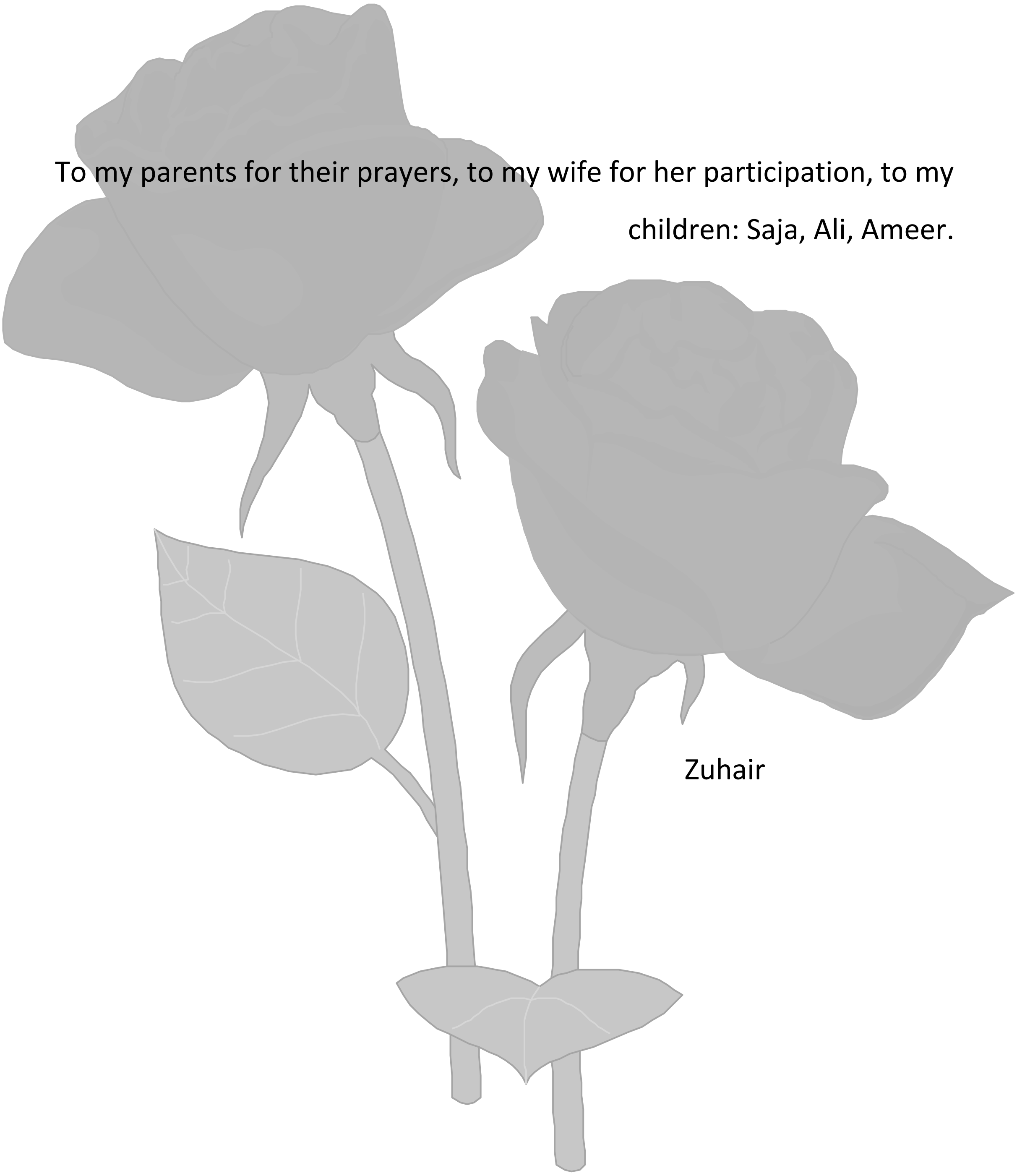

To my parents for their prayers, to my wife for her participation, to my children: Saja, Ali, Ameer.

Zuhair

Praise be to God at first

I would like to express my deep appreciation and sincere thanks to Chief Res. Dr. J.K. Ahmad & Assist Prof. Dr. Tahseen A. AL-hattab / Babylon University for their active valuable supervision.

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Abstract

The aim of this work proposal is using a natural pigment extracted from plants such as (chlorophyll, carotene, and anthocyanin) as colorants, stabilizers, and plasticizers for certain polymers such as (epoxy resin ER, unsaturated polyester UPE, and polyvinyl chloride PVC). This suggeston depends on their role in life as a light absorber, colorant and catalyst in the photosynthesis.

Natural pigment extracted by a simple method it is suitable to be a commercial extraction process and prepared polymer samples with different ratio of pigments, and many tests were executed such as environmental stability, UV-spectroscopy, tensile, flexural, impact, and hardness tests to study effect of pigment on the polymers properties.

The results show that chlorophyll protects the above polymers against heat, UV, and environmental effects in which polymers exposed to these tests. It seems that chlorophyll acts as the protector material to the polymers. The weight losses are the indicator for the above condition. The improvement percent in weight loss for blank samples and mixed samples with chlorophyll when exposed to following condition are as follows:

-١٢٠°C and ٢١ days: the improvement percent ٢١٢, ١٧, and ٧.

-UV-radiation: the improvement percent ٥١, ٣

-environmental stability: the improvement percent

for the ER, UPE, and PVC

..

and ٣٩٢.

The anti degradation improvement in PVC when exposed to ١٣٠°C was ٧١.٤٪ extra time with chlorophyll than time with PVC alone.

For all above tests, these pigments show permanent color with the polymer.

The low percent (by weight) of chlorophyll (less than ٠.٢٪) results in increasing mechanical properties of the polymers due to increase the interaction between the polymer molecules and chlorophyll, this supported by UV spectra measurements which show an interaction with the lone pair of electron in chlorophyll molecules.

At high chlorophyll percent (more than ٠.٢٪) the mechanical properties decreases except the impact increase because chlorophyll acts as a plasticizer at such percent which interferes between the molecules of the polymers and destroying the interaction between polymer molecules i.e. it acts as a lubricant to facilitate the movement of the polymer macromolecules chain over each other and provides internal lubricity. By the same mechanism, hardness decreases while the impact increases. The percent improvement in hardness was ٣٠, ٧٩, and ٥٠٪ for the ER, UPE, and UPVC respectively. While in the impact was ٢١, ٢٦ for the ER and UPE respectively. Comparing with the available literature, our results show that the improvement in toughness obtained with a low chlorophyll percent (٤-١٠٪) comparing with around ٥٠٪ of other plasticizers appear in literature.

Mechanical tests for samples exposed to heat, UV, and environmental condition for different time show regular results with chlorophyll than with blank samples, this indicates that chlorophyll acts as a shield to protect the polymer against the random change comparing with the blank samples.

Anthocyanin shows similar behavior to the chlorophyll. Each of them has functional groups that interact with polymer. While in the case of carotene, a completely different behavior is shown in which all mechanical properties decreases, this is due to the absence of the strong functional group as well as it is known in literature as a fatty pigment.

This work exits with a good replacement for commercially available synthetics colorants, stabilizers, and plasticizers avoiding their toxicity and their highly cost.

Abbreviation

ASTM	American standard for testing material
A	Cross section area
A	Absorbance
CRPEHA	Carboxyl randomized poly (٢-ethyl hexyl acrylate)
c	Light speed
CTBN	Carboxyl – terminated polybutadiene – acrylonitrile copolymer
DEHP	Diethylhexyl – phthalate
ERPEHA	Epoxy randomized poly (٢- ethyl hexyl acrylate)
EVA	Ethylene – vinyl acetate copolymer
ER	Epoxy resin
E	Energy
E	Modulus of Elasticity
EtOAc	Ethyl acetate
FTIR	Fourier-Transform Infrared
HDPE	High density Polyethylene
HPLC	High Performance Liquid Chromatography
h	Planck’s constant

IPP	Isotactic polypropylene
I	Second moment of inertia
$I.$	Intensity of the incident radiation
I	Intensity of the transmitted radiation
k	Thermal conductivity
LDPE	Low density polyethylene
M	Bending moment
MeOH	Methanol
NASA	National Aeronautics and Space Administration
PAE	Dialkyl phthalate
PVA	Poly (Vinyl acetate)
PMMA	Poly (methyl methacrylate)
PBT	Poly (butylenes terephtalate)
PVC	Poly (Vinyl chloride)
PU	Polyurethan
q	Quantity of heat / second
T	Transmittance
t	Time
T_m	Melting point
T_g	Glass transition temperature
UPE	Unsaturated polyester resins
UPVC	Un plasticized Poly (Vinyl chloride)
UV	Ultraviolet
$\Delta T/\Delta X$	Temperature gradient

Symbols

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Introduction

Chapter Two

Theoretical part

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الخلاصة

ان الهدف من هذا البحث هو اقتراح استخدام صبغات طبيعية مستخلصة من النباتات مثل (الكلوروفيل والكاروتين والانثوسيانين) كمواد ملونة colorants ومثبتة stabilizers وملدنة plasticizers لبعض البوليمرات مثل (راتنج الايبوكسي ER والبولي استر الغير مشبع UPE والبولي فينيل كلورايد PVC) . يعتمد هذا الاقتراح على دورها في النبات كماصة للضوء ومحفزة في التركيب الضوئي .

الصبغات النباتية استخلصت بطريقة مبسطة يمكن ان تكون عملية استخلاص تجارية, وتم تحضير عينات بوليمرية وبنسب مختلفة من الصبغات و اجريت العديد من الاختبارات مثل الاستقرار البيئي وقياس طيف UV والشد والانثناء والصدم واختبار الصلادة لدراسة تاثير تلك الصبغات على خواص البوليمرات.

بينت النتائج امكانية الكلوروفيل على حماية البوليمرات اعلاه من تاثير الحرارة والاشعة فوق البنفسجية UV والظروف الجوية عند تعرض البوليمرات لهذه الاختبارات. واخذ الفقدان بالوزن كمؤشر على الحالات اعلاه. فنسبة التحسن بالفقدان بالوزن عند مقارنة عينات بوليميرية محتوية على الكلوروفيل باخرى غير محتوية عليه عند تعرضها للظروف التالية كان كما يلي:

- ١٢٠ ^{o}C لمدة ٢١ يوم : نسبة التحسن كانت ٢١٢, ١٧, ٧.
- التعرض للاشعة فوق البنفسجية : نسبة التحسن كانت ٥١, ٣٥, ٤٣.
- التعرض للجو : نسبة التحسن كانت ٢٦٠, ٢٨٢, ٣٩٢.

لكل من PVC, UPE, ER على التوالي.

التحسن في مقاومة التحلل للبولي فينيل كلورايد عند التعرض لدرجة ١٣٠ ^{o}C كانت ٧١.٤ % زيادة بالوقت اللازم لتحلل عينة محتوية على الكلوروفيل نسبة الى وقت العينة الخالية منه, مع ملاحظة تحت كل ظروف الاختبارات اعلاه اظهرت الصبغات لون ثابت في البوليمرات.

عند نسب منخفضة من الكلوروفيل (اقل من ٠.٢٪) الخواص الميكانيكية للبوليمرات تزداد يعود ذلك الى زيادة الترابط بين جزيئات الكلوروفيل وجزيئات البوليمر والذي اؤكد من خلال قياسات اطياف الاشعة الفوق البنفسجية UV والتي اظهرة الترابط مع قمة peak لزوج الكتروني lone pairs في جزيئات الكلوروفيل.

عند النسب العالية من الكلوروفيل (اكثرمن ٠.٢٪) الخواص الميكانيكية للبوليمرات تنخفض عدى مقاومة الصدم تزداد لكون الكلوروفيل يعمل كملدن عند مثل هذه النسب والتي تتداخل بين جزيئات البوليمر وتضعف الترابط بينها . وهذا يعني عملت الصبغات كمادة مزيتة تسهل حركة السلاسل الجزيئية الدقيقة على بعضها . وبنفس الميكانيكية الصلادة تقل بينما مقاومة الصدم تزداد , فنسبة التحسن في الصلادة كانت ٣٠٪, ٧٩٪, ٥٠٪ لكل من UPVC, UPE, ER بينما في مقاومة الصدم كانت ٢١٪, ٢٦٪ لكل من UPE, ER على التوالي .وبالمقارنة مع البحوث المتاحة النتائج اظهرت تحسن في المتانة مع نسب منخفضة (٤-١٠٪) مقارنة مع القيم المذكورة في البحوث والتي تصل الى حوالي ٥٠٪ .

الخواص الميكانيكية لعينات عرضت الى الحرارة والاشعة فوق البنفسجية UVوالظروف الجوية لاوقات مختلفة اظهرة نتائج اكثر انتظاما مع الكلوروفيل مقارنة مع العينات الغير محتوية عليه. وهذا مؤشر على ان الكلوروفيل عمل كدرع لحماية البوليمر ضد التغيرات العشوائية عند التعرض لمثل هذه الظروف .

الانثوسيانين اظهر سلوك مشابه للكلوروفيل لان كلاهما يحتوي على مجاميع فاعلة والتي تتفاعل مع البوليمر , بينما في حالة الكاروتين سلوكه مختلف تماما والذي يظهر من خلال انخفاض الخواص الميكانيكية وذلك راجع الى غياب المجاميع الفاعلة القوية كما انها معروفة كصبغات دهنية.

يخرج البحث ببديل جيد للملونات والمثبتات والملدنات الصناعية والمستخدمة حاليا لتجنب سميتها وكلفتها المرتفعة.

Chapter One

Introduction

١.١ Introduction:

This research is planning to extract some natural plant pigments by a simple method to use these pigments as additives, colorant, stabilizers, and plasticizer (as UV- visible light absorbers) for the same polymers as safety natural materials instead of unsaffy industrial additives which had already side effect on the environment.

This research deals with the above pigments from different points of view:

١. As Colorants: Since colorants are fine distributed particles in molecular range (dyes) or in the rang of ٠.١-١ micron (pigments) which absorb the complementary color from the desired color of the incident white light. These natural pigments have a permanent color under the four season's repletion through the plants life, thus, it was thinking in their using for this goal in different concentrations to get different color shades.

٢. As Stabilizers: Since these materials are colored, that means they absorb all light except the color that appears on each of them, well, as these pigments are organic or organometallic materials with multifunctional groups, thus, certainly they also absorb the harmful UV-light i.e. it is possible to act as protectors for polymers against deformations. A stabilizer which prevents the elimination of hydrogen chloride from polyvinyl chloride.

٣. As Plasticizers: Since these materials are relatively large molecules with branches and multifunctional groups beside that, some of them have oily appearance, and according to the two theories of plasticizing (lubricity and the gel theories), thus, it is hoped that they may be interfere between the chain molecules of the plastic and break the attachment and extending the distance between neighbored molecules and results in increasing in workability and flexibility or distensibility.

١.٢ Introduction to Engineering Polymers:

People have been using for thousands of years, Rubbers, Silk, Cellulose, and much more of nature's most useful materials, which are polymers. The first true synthetic polymers were prepared in the early ١٩٠٠s by using phenol and formaldehyde to form resins – Baekelands Bakelite [١,٢].

Experiments indicated that polymers had a molecular weight so unusually large that it was not believed that this could be due to one single molecule. Most scientists, therefore, believed that polymers were composed of a large number of small molecules that somehow stick together in colloidal aggregates, thus, it gives the false impression of large molecules. The first scientist to challenge this aggregate theory was the German scientist Hermann Staudinger in the beginning of the ٢٠-th century. He argued that polymers were made of single chain-like molecules, consisting of repeating units (monomers) linked by covalent `bonds Fig. (١-١). Staudinger proposed the name macromolecules for these giant molecules. At first, Staudinger's theory was received with much skepticism. It was only accepted by most scientists after the work of Carothers, who succeeded to create a synthetic macromolecule (which we now know as nylon) in his laboratory, and that of Mark and Meyer who proved the macromolecular structure of many natural polymers using x-ray crystallography. In the ١٩٥٠s, Ziegler and Natta's work on anionic coordination catalysts led to the development of polypropylene; high-density, linear polyethylene; and other stereospecific polymers [٣,٤].

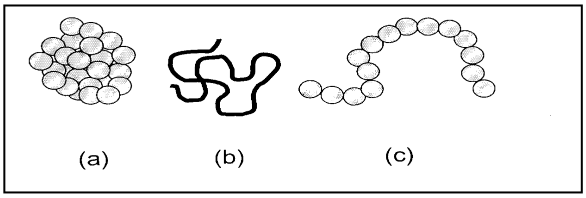


Figure (١-١):schematic depiction of (a) the historical view of a polymer as a colloidal aggregate, (b)a polymer as a macromolecule with covalently linked subunits, and
(c)a supramolecular polymer with non-covalent bonds between the subunits[٤].

١.٣ Properties and Applications of Polymers:

Plastics are an important part of everyday life; products made from plastics range from sophisticated articles, such as prosthetic hip and knee joints, to disposable food utensils. One of the reasons for the great popularity of plastics in a wide variety of industrial applications is the tremendous range of properties exhibited by plastics and their ease of processing. Plastic properties can be tailored to meet specific needs by varying the atomic composition of the repeat structure; and by varying molecular weight and molecular weight distribution. The flexibility can also be varied through the presence of side chain branching and according to lengths and polarities of the side chains. The degree of crystallinity can be controlled through the amount of orientation imparted to the plastic during processing, through copolymerization, by blending with other plastics, and via the incorporation of an enormous range of additives (fillers, fibers, plasticizers, and stabilizers). Given all of the avenues available to pursue in tailoring any given polymer, it is not surprising that the variety of choices available to us today exists [٥,٦].

١-٤ Extraction of Plants Contents:

The precise mode of the extraction naturally depends on the texture and water content of the plant material being extracted and on the type of substance that is being isolated. In general, it is desirable to `kill' the plant tissue, i.e. prevent enzymic oxidation or hydrolysis occurring, and plunging fresh leaf or flower tissue, suitably cut up where necessary, into boiling ethanol is a good way of achieving this end. Alcohol, in any case, is a good all-purpose solvent for preliminary extraction. Subsequently, the material can be macerated in a blender and filtered but this is only really necessary if exhaustive extraction is being attempted. When isolating substances from green tissue, the success of the extraction with alcohol is directly related to the extent that chlorophyll is removed into the solvent and when the tissue debris, on repeated extraction, is completely free of green colour, it can be assumed that all the low molecular weight compounds have been extracted.

The classical chemical procedure for obtaining organic constituents from dried plant tissue (heartwood, dried seeds, root, and leaf) is to continuously extract ; powdered material in a Soxhlet apparatus with a range of solvents (see fig. ١-٢), starting in turn with ether, petroleum and chloroform (to separate lipids and terpenoids) and then using alcohol and ethyl acetate (for more polar compounds). This method is useful when working on the gram scale. However, one rarely achieves a complete separation of constituents and the same compounds may be recovered (in varying proportions) in several fractions.

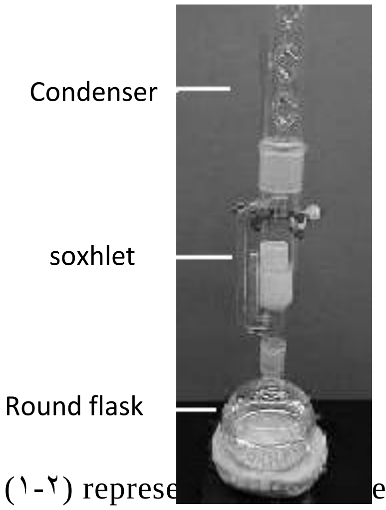


Figure (١-٢) represe extraction apparatus [٧].

The extract obtained is clarified by filtration through celite on a water pump and is then concentrated in *vacuo*. This is now usually carried out in a rotary evaporator, which will concentrate bulky solutions down to small volumes, without bumping, at temperatures between ٣٠ and ٤٠°C. Extraction of volatile components from plants needs special precautions.

There are short-cuts in extraction procedures which one learns with practice. For example, fallen isolating water-soluble components from leaf tissue, the lipids should, strictly speaking, be removed at an early stage, before concentration, by washing the extract repeatedly with petroleum. In fact, when a direct ethanolic extract is concentrated on a rotatory evaporator, almost all the chlorophyll and lipid are deposited on the side of the flask, and, with skill, the concentration can be taken just to the right point when the aqueous concentrate can be pipetted off, almost completely free of lipid impurities.

The concentrated extract may deposit crystals on standing. If so, these should be collected by filtration and their homogeneity tested for by chromatography in several solvents.

If a single substance is presented, the crystals can be purified by recrystalization and then the material is available for further analysis. In most cases, mixtures of substances will be presented in the crystals and it will then be necessary to redissolve them in a suitable solvent and separate the constituents by chromatography. Many compounds also remain in the mother liquor and these will also be subjected to chromatographic fractionation. As a standard precaution against loss of material, concentrated extracts should be stored in the refrigerator and a trace of toluene added to prevent fungal growth.

When investigating the complete photochemical profile of a given plant species, fractionation of a crude extract is desirable in order to separate the main classes of constituent from each other, prior to chromatographic analysis. One procedure based on varying polarity that might be employed on an alkaloid-containing plant is indicated in Fig.(١-٣) The amounts and type of compounds separated into the different fractions will, of course, vary from plant to plant. Also, such a procedure may have to be modified when labile substances are under investigation [٧].

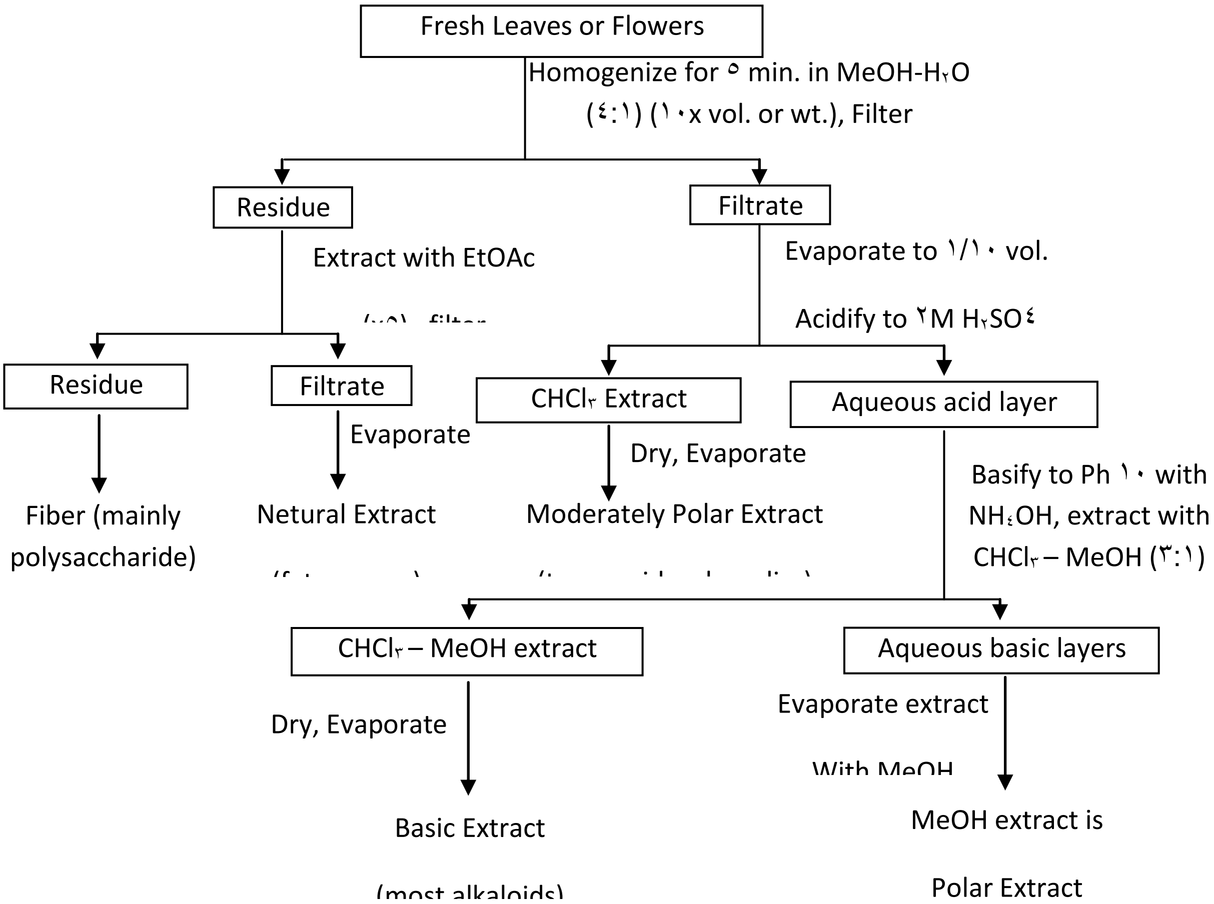


Fig. (١-٣) A general procedure for extraction fresh plant tissues and

١-٥ Plant Pigment and Human Health:

These pigments have been implicated in regimes to maintain human health, to protect against chronic disease incidence, or to restore wellness by repairing tissues after disease has been established.

These natural pigments and related photochemicals are integral to the plant’s strategies for survival, serving protective roles (as shields against a biotic stresses like temperature, UV-B radiation, low water potential, or mineral stress)[٨].

١-٥-١ Radiation protection with chlorophyll and Human Health:

The chlorophyll molecule has the unique capacity to convert the energy of the sun into chemical energy. The structures of chlorophyll and heme are shown on the Fig. (١-٤) obviously, the two structures are similar. The most apparent difference between them is that the porphyrin ring of hemoglobin is built around iron, while the porphyrin ring of chlorophyll is built around magnesium.

After an exhaustive review of the scientific research relating chlorophyll to blood, it is concluded that the relationship between the two is much more complex, and indeed more beautiful, than the simple idea of the body's substituting an iron molecule for a magnesium molecule to make hemoglobin from chlorophyll [٩,١٠].

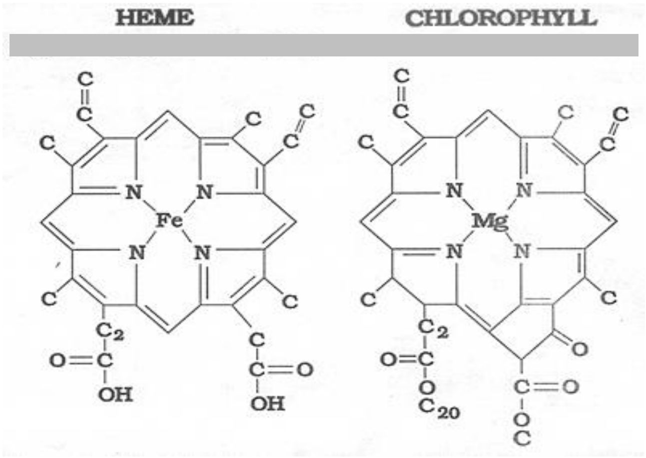


Figure (١-٤) Similarity of the chemical structures of heme and chlorophyll molecules [٩].

There is scientific evidence that chlorophyll offers protection from radiation damage in testing animals. This information has been reported in the scientific literature since the early ١٩٥٠s. Early reports showed that certain vegetables significantly reduced mortality in rats exposed to lethal doses of X – rays. In ١٩٦٢s, Doris Calloway and her colleagues gave lethal doses of X – radiation to healthy guinea pigs whose standard diet had been supplemented with a carefully controlled variety of foods and nutrients. Ninety – seven percent of the animals given no vegetable supplements died within twenty days [١١-١٣].

١-٥-٢ Anthocyanins:

Anthocyanins belong to water-soluble plant pigments. They are derivatives of ٢-phenylbenzopyrylium. Due to the commonness of occurrence (among others in fruit) they are components of human diet. Owing to scientific research they have become not only food products but also therapeutic agents. They exhibit, among others, antioxidative and anti-inflammatory activity, they also show favorable effect in the treatment of some types of neoplasms[١٤,١٥].

Antioxidative properties of anthocyanins are used, among others, in the therapy of cardiovascular diseases. Anthocyanins decrease the amount of

oxidized, show antiaggregative and vasodilating activities and, by inhibition of free radical formation in the process of reperfusion. Anthocyanins are able to decrease the activity of nitric oxide syntheses and the level of nitric oxide. Anthocyanins applied with other antioxidants act photoprotectively upon exposure of experimental animals' skin to UV radiation [١٦,١٧].

١-٥-٣ Carotenoids:

In terms of nutraceutical contribution, carotenoids are best recognized for their antioxidant capacity, especially in the membranes, since they are pigments located within membranes. Hydrogen peroxide, singlet oxygen, nitrogen oxides, superoxide anion, and other reactive oxygen species insulting the body from either endogenous or exogenous routes (and thus aggravating to a plethora of chronic human disease conditions) can be inactivated by carotenoids; in fact, carotenoids are considered the most potent of biological quenchers of singlet oxygen, and can react with virtually any radical species likely to be encountered in a biological system. In the majority of these reactions, the carotenoids break down to biologically active degradation products. The carotenoids lycopene, lutein, and zeaxanthin are excellent antioxidants and oral sun protectants that protect exposed tissues from light-induced damages [١٨-٢١].

١.٦ Literature Review:

Extensive studies on polymer additives and the effect of these additives on physical and mechanical properties and polymer degradation behavior.

Mc Neill and etal. (١٩٨٤) examined the effect of silver acetate, ammonium polyphosphate, and Zinc bromide on Poly (methyl methacrylate) (PMMA) degradation. These additives combined with PMMA lead to a severe destabilization of the polymer and depolymerization [٢٢].

Robson F. Storey and etal. (١٩٨٥) studied the improved room temperature cure of unsaturated polyester resins by mixed with benzoyl peroxide, and showed that added ٠.١٪ benzoyl peroxide reduced the cure time from ٣٥ min. to ١٥ min. [٢٣].

N.A. Halim (١٩٨٨) used accelerated weathering test which was carried out to study the effect of degradation on mechanical and optical properties of Low density poly ethylene (LDPE), Ethylene – vinyl acetate copolymer (EVA), and blend film of LDPE/ Isotactic polypropylene (IPP). Results of mechanical properties indicated that degradation has started during the first ٢٥٠ hours of aging. All the results obtained were explained in terms of structural and morphological changes occurring as a result of the UV radiation and thermal aging [٢٤].

C.E. Hoyle and etal. (١٩٩١) explained the effect of the use radiation on the degradation of polyimides .Polyimide undergo facile and sestructive (Chain – breaking) changes upon photolysis with an unfiltered medium-pressure mercury Lamp source. One of the initial photochemical reactions is probably a carbonyl-nitrogen bond cleavage between the carbonyl carbon and nitrogen in the imide linkage [٢٥].

Charles A. and etal. In the same year, thay studied the thermal degradation of PMMA, in the presence of $MnCl_{۲}$. There are both advantages and disadvantages to the use of $MnCl_{۲}$ as a flame retardant. $MnCl_{۲}$ pronotes an initial depolymerization of the polymer and thus promotes burning [۲٦].

M. Paauw and etal. (۱۹۹۳) used the FTIR method for the one-step quantitative analysis of simple unsaturated polyester resins (UPE). It is of interest to examine the resin when this is composed of a single glycol or of two glycols in combination [۲۷].

I. Arvanitoyannis and etal. (۱۹۹۳) studied the correlation between food and drug synthetic dyes with plastic materials used for packaging. Synthetic dyes as food additives has some undesirable consequences such as bleeding of dyes between food components or migration into the packing material and , also , problems caused by interactions between food colorants and packaging material that result in an unappetizing and unsanitary looking product[۲۸].

M. C. Gupta and etal. (۱۹۹۷) thermal degradation of Poly (Vinyl chloride) (PVC) has been studied in presence of metal oxides by a thermogravimetric method. It follows a two-step mechanism. In the first step chlorine free radical is formed as in the case of pure PVC, and in the second step chlorine free radical replaces oxygen from metal oxide to form metal chloride and oxygen free radical subsequently , the oxygen free radical abstracts hydrogen from PVC. Formation of metal chloride is the rate – controlling step. The metal chlorides formed during the thermal degradation either volatilize or decompose simultaneously to lower metallic chlorides depending on the boiling point or the volatilization temperature [۲۹]. This result agrees with ***Nandhan and Ravi v. (۲۰۰۵***) who showed the degradation of polymers with Various metal oxides such as ZnO , $Fe_{۲}O_{۳}$, $Co_{۳}O_{٤}$,and $TiO_{۲}$ and metal chlorides such as $AlCl_{٣}$,$ZnCl_{٢}$,$FeCl_{٣}$,and $CoCl_{٢}$. This research explained the increased degradation with the presence metal compounds due to the high reactivity of chlorine radical or hydrogen chloride which lead to the destabilization of polymers [٣٠].

Ljubomir Misev and etal. (١٩٩٩) studied the UV – Curable powder coating based on an UPE binder and a vinyl ether cross linker has been tested for weathering resistance. Accelerated and outdoor weathering demonstrate impressively the combined protective action of a UV absorber a hindered a mine light stabilizer. Successful cure of coatings of various colors and shades from organic and inorganic pigments is also reported in the present study. Curing performance mainly depends on pigment absorption and particle size [٣١].

Young Lee and etal. (٢٠٠١) explained the characteristics of thermal degradation of epoxy system filled with natural Zeolite. Found that the activation energy at ٢٠ phr of zeolite was lower than that at any other content of Zeolite and these values decreased with the increment of heating rate [٣٢].

Tatsuhiro Niino and etal. (٢٠٠١) studied the hydrolysis of dialkyl phthalate migration from PVC and monoeste formation in human saliva. PAE are widely used as plasticizers to impart softness and flexibility to normally rigid plastics such as PVC. Medical devices and toys are often made of PVC containing the predominant plasticizers. Some plasticizer have induced testicular toxicity and other effects such as many structurally dissimilar compounds known as peroxisome proliferators induce tumors in the liver and orally – ingested Dialkyl phthalate (PAE) is hydrolyzed to its monoester by endogenous esterases of many tissues , such as the small intestine . Monoesters are though to be more hepatocarcinogenic than their parent compound [٣٣].

M. A. Salem (٢٠٠١) work covered the effect of UV-rays on the mechanical properties of LDPE films pigmented with carbon black and titanium dioxide in different formulations, and showed that the use of both pigments in appropriate concentration ratios give a reliable improvement in the mechanical and physico – chemical properties of LDPE films exposed to UV-radiation [٣٤].

Jordan and etal. (٢٠٠١) determined kinetic parameters, the dehydrochlorination of PVC, using thrmogravimetric analysis, they were; order of apparent activation and factor of apparent frequency, four different degradation mechanisms were deduced, final dehydrochlorination, random chain scission, ciclization and coke. Also demonstrated that this type of degradation is critical during the process of manufacture of PVC, when the same is melted and soon after extruded. The degraded polymer loses its plasticity, passing to a rigid composition [٣٥].

Alaa Al-Zabiady (٢٠٠٢) studied the effect of temperature, humidity and UV on the properties of the natural rubber and the synthesis rubber in which crude natural and synthesis rubber simple are exposed to temperature range ٤٠ -٨٠ °C for ٢-٣٠ days and compared the mechanical and physical properties of exposed and unexposed sample [٣٦].

Luiz G. M. and etal. (٢٠٠٣) demonstrated that the thermal and for UV degradation induce fragility to the material, but the quantification of these levels of degradation is not available. The embrittlement could be translated by the loss of mass or through the loss of hydrogen chloride and the consequent sprouting of double bonds. This work tries to demonstrate the changes in the properties caused by to display of the samples to temperature levels and global solar radiation , for several periods of time [٣٧].

Jason Leadbitter and etal. (٢٠٠٣) studied the main additives that can be incorporated in PVC for useing the typical food packaging applications. They showed that, only organo – tin and calcium/zinc stabilizers can be used in food packaging application, and the main type of plasticizers used in food packaging is the adipates [٣٨, ٣٩].

G. Sivalkingam and etal. (٢٠٠٣) studied the role of metal oxides on thermal decomposition of PVC and PVA and their blends. While the degradation of PVA was mildly affected by the presence of metal oxides, the degradation of PVC was greatly influenced by metal oxides. FTIR studies after the first stage showed the disappearance of the C – Cl of PVC and C = O and C– O groups of PVA, suggesting the formation of a polyolefinic chain [٤٠].

A. Zh. Makhkamov and etal. (٢٠٠٤) studied the chemical composition of the fatty mass representing a waste from the oils and fats industry. It has been shown that the fatty acids, the ١٨: ٢ species possesses, a pronounced stabilizing action on polymers, and of polyolefins the least oxidized part of the gossypol pigments, while the fatty mass is a more effective stabilizer than its individual components [٤١].

Sandra Steingrater (٢٠٠٤) studied environmentally hazardous throughout PVC lifecycle (production, use, and disposal). Dioxin a known human carcinogen, is created during the production of PVC feedstocks, as well as when PVCs are burned in waste incinerators. Among other things, dioxin has been linked to endocrine disruption, reproductive abnormalities, neurological problems, and infertility in humans and animals. In addition, large amounts (up to ٦٠percent of the final product by weight) of chemicals called "Phthalates" are used to manufacture PVC products. A commonly used phthalate plasticizer called diethylhexyl – phthalate (DEHP) is a probably reproductive toxicant, as well as, a toxicant of the liver and kidney. Lead and other heavy metal such as cadmium and organo-tins which added to PVC as a stabilizers, metal stabilizers are highly toxic [٤٢].

P. Budrugeac and etal. (٢٠٠٥) presented the results of non – isothermal kinetic analysis of the thermooxidative degradation in air and oxygen of an up resin is presented. It has been shown that the thermooxidative degradation in oxygen occurs at lower temperatures that the thermooxidative degradation in air. The kinetic parameters of the thermooxidative degradation depend on the heating rate and the oxygen pressure [٤٣].

Jamina Gabrielska and etal. (٢٠٠٥) compared the antioxidant abilities of anthocyanins with water – soluble tocopherol derivative, trolox. They found that the antioxidant activity of all the anthocyanins studied was higher than that of trolox [٤٤].

Nächste Meldung (٢٠٠٦) studied the light – protection for food packaging by using chlorophyll pigment. The combination of the oxygen and light causes various ingredients to undergo photo – oxidation. Dying plastic films and bottles by using chlorophyll for packaging material remains almost transparent yet they filter out light in the critical wavelength ranges. With chlorophyll the food can be stored for a considerably longer period of time under exposure to light.

Using chlorophyll not only serves to emphasize the olive – green tone – the oil can also be stored for a considerably longer period of time under exposure to light. The institute's scientists have already been able to dye by chlorophyll a whole range of different plastic materials used for packaging foodstuffs. To do this they employ a wide range of techniques: depending on the type and thickness of the film and the desired intensity of color, the chlorophyll is either added to the raw plastic prior to processing or it is applied to the prepared film as a coating. In multi – layered composite films it is incorporated into the laminating adhesives. There are also plans to develop printing inks containing the natural pigment [٤٥].

Umoren S. A. and etal. (٢٠٠٦) studied the effect of monoazo dye on the mechanical properties of LDPE and unplasticized Poly (Vinyl chloride) (UPVC). It was shown that the elongation at a break increases for colored UPVC and decreases for colored LDPE as the dye uptake increase. The increase in elongation at a break may be an indication that the dye is exercising a plasticizing action. Although the mechanism through which this occurs, is not known, it may be due to the interaction between the solvent and the dye, thus, causing the latter to act as a lubricant to facilitate movement of UPVC macromolecules chain over each other and provides internal lubricity. This can be a significant advantage indicating that the dye can function as a dual purpose polymer ingredient. The possibilities being as a colorants and a plasticizer.

The dye has no significant effect on the ultimate tensile strength of UPVC while at ١٪ wt composition, the dye upgrade the modulus of LDPE and downgrades between ٢-٥٪. The decrease in mechanical properties may due to the decrease in intermolecular forces between the polymer molecules [٤٦].

G. Woodall and etal. (٢٠٠٦) stated that the role anthocyanins play in UV protection was assessed in juvenile leaves of two syzygium species, which contain high anthocyanin concentration. HPLC was used to separate UV – absorbing anthocyanins from other soluble UV – absorbing phenolic compounds. The results suggest that the UV protection hypo thesis is not valid for anthocyanins injuvenile syzygium leaves [٤٧]. At the same year ***R. E. Wrolstad*** studied the effect of UV – radiation on plants, which showed that the anthocyanin pigment gives protection against the harmful effects of UV irradiation [٤٨]?

Thermosets polymers are widely used in application such as coating and as a matrix material for making many composites. However, it is brittle in nature and has poor resistance to crack propagation, so we found many researcher works on improving toughness of the thermoset polymer.

Bascom and etal. (١٩٨٩) their work covered the effect of elastomer concentrations – modified epoxy on mechanical properties [٤٩].

P. Sasidharan A. and etal. (١٩٩٠) investigated the shear strength for Epoxy resin(ER) containing varying a mounts of Carboxyl – terminated polybutadiene – acrylonitrile copolymer (CTBN). It was observed that as CTBN content increased shear strength increased significantly and passed through a maximum at about ١٠ parts CTBN content per ١٠٠ parts ER and then decreased. At the higher CTBN content, the rubber phase became continuous, and the system exhibited a fall in mechanical properties [٥٠].

Ojin kwon (١٩٩٨) the phase separation process of a rubber modified epoxy system during cure was analyzed by a model developed on the basis of thermodynamic description of binary mixture and constitutive equations for nucleation and growth rates. As ER are cured, rubber molecules are precipitated from the ER to a non- equilibrium composition due to the decrease in the configurational entropy and the increase in the viscosity with conversion[٥١].

In the same year ***Grog P. Smestad*** used the flavonoids such as anthocyanins and chlorophyllides as sensitizer for the nanocrystalline solar cell[٥٢].

P. A. Lovell and etal. (٢٠٠٠) investigated the mechanical properties of rubber – toughened polyester resins showed that, the tensile properties were found to be dependent primarily on particle content. The toughened materials showed greater ductility with Young's modulus decreasing and fracture strains increasing with particle content. The increase in toughness was found to be dependent on particle weight fraction, the chemistry of the rubbery phase and the rate of fracture[٥٣]. In that way and in same year ***Bobby Russell*** improved ER toughness by added rubber[٥٤].

Jörg Fröhlich and etal. (٢٠٠٣) they used the Epoxy as matrix material for hybrid nanocomposites containing both inorganic nanofiller and compatibilized polyether liquid rubbers. They found that without compatibilization, the rubber dose not phase separate and flexibilizes the epoxy resin. The stearate compatibilizer is sufficient to achieve phase separation of the rubber. This compatibility matching represents the key to novel phase – separated nano composites with significantly improved toughness and only marginally tower stiffness[٥٥].

S. Kar and etal. (٢٠٠٤) studied Epoxy / Liquid rubber composition. The effect of toughened concentration on the adhesive and impact properties for both filled and unfilled aluminum silicate. Improved properties were obtained for epoxy resins toughened with (١: ١) mixture of Carboxyl randomized poly (٢-

ethyl hexyl acrylate) (CRPEHA) and Epoxy randomized poly (٢- ethyl acrylate) (ERPEHA) of filled epoxy resins was higher than that of unfilled ones [٥٦].

Robert Y. T. and etal. (٢٠٠٤) studied the fracture energy of an elastomer – modified epoxy polymer as a function of loading rate. Fracture tests were carried out by using compact tension specimens and standard izod impact specimens. The fracture energy of the base epoxy was increased by the elastomric additives. The extent of increase, however, was found to decrease with increasing loading rate [٥٧]. In that year ***K. P. Ochathervar Mahesh*** explained the interpenetrating polymer networks of bismaleimide – modified

Polyurethane – epoxy systems. The results obtained from these studies indicate that the incorporation of polyurethane into epoxy increases the mechanical strength and decreases the thermal properties of epoxy resin. Where as the incorporation of chain – extended bismaleimide into polyurethane – modified epoxy system increases the tensile and flexural properties and thermal stability and decreases the impact strength according to its percentage content [٥٨].

D. S. Kim and etal. (٢٠٠٤) the effects of particle size on the fracture toughness of PU/UPE were studied in this work. They investigated that a ١.٩ times increase in fracture toughness of UPE was achieved with the formation of cavitated particles [٥٩].

Peter L. Drazal and etal. (٢٠٠٥) studied the nanomechanical properties of UV degraded $TiO_٢$ /Epoxy nanocomposites. It was shown that the addition of nanoparticles (diameter ٢٠-٢٥٠ nm) increased the elastic modulus of the epoxy. Exposure to UV radiation increases the elastic modulus of the nanocomposite . The rate of increase in the elastic modulus was reduced with increasing volume fraction of nanoparticles [٦٠].

G. A. Crosbie and etal. (٢٠٠٥) made an investigation into the microstructures of two polyester resin systems, with reactive liquid rubber additions incorporated. Rubber additions modified the mode of fracture observed in double torsion test of polyester resins, from continuous crack propagation to slip-stick, and distinctive changes in fracture surface morphology were observed. In zones of crack arrest and slow stable crack growth, crack blunting occurred and highly deformed structures were seen on the fracture surface [٦١].

D. Behera and etal. (٢٠٠٥) developed a method provided a simple and practical solution to improving the toughness of a cured epoxy by incorporation Phenol – nonyl phenol (PNPF) based polymer at different concentrations. The impact and adhesive strengths of the unmodified and modified epoxy networks were characterized. The modified of epoxy resin using PNPF showed significant enhancement of impact and adhesive strengths over the unmodified one. The modification caused the formation of a chemical linkage between PNPF and ER which led not only to a phase separation, but also to formation of intrinsically strong chemical bands across the PNPF phase / resin matrix interphase, which was the main cause of the improved impact and adhesive strengths. The optimum results were obtained at ١٠ Phr of modifier [٦٢]. In ***(٢٠٠٦) Viviane Goncalez and etal.*** worked in the same way.They studied the mechanical properties of epoxy; networks have been modified with block copolymers prepared by pre-reacting functionalized Polybutadiene with the epoxy resin. Improvement of the impact resistance with ١٠ Phr rubbers (above this optimum rubber content, a fall in the impact strength, because of the presence of rubber particles homogeneously dispersed inside the epoxy matrix [٦٣].

Christors C. C. and etal. (٢٠٠٦) the structural integrity of combinations of graphite and glass fibers with a toughened ER matrix under dynamic impact loading was investigated in this work. Results show the damage progression sequence and the changes in the structural response characteristics due to dynamic impact. The fundamental premise of computational simulation is that these completes evaluation of composite fracture requires an assessment of ply and supply level damage / fracture processes as the structure is subjected to loads [٦٤].

H. V. Ramakrishna and etal. (٢٠٠٦) used PBT and Granite powder to improve the mechanical properties of ER. The tensile , flexural , compressive , and impact strength are maximum when the PBT content is ٢٪ in the blend , and the composites with ٥٠٪ granite powder showed better properties [٦٥].

١-٧ The Aim of This Work:

The aim of the present Work is applying natural pigments. The objective is achieved from two steeps, the first one is selection of these pigments according to their physical and chemical properties such as light absorbers, and relatively large molecules with multi functional groups enable them to behave as plasticizers and the second is studying the effect of natural pigments such as Chlorophyll, β-Carotene, and Anthocyanins as colorants, stabilizers, and plasticizers for widely used polymers such as PVC, ER, and UPE by preparing different type of samples with different weight percent of pigments and testing samples by physical, chemical and mechanical tests.

Chapter Two

Theoretical part

٢-١ Polymers:

Polymer is composed of the two Greek words poly and mer, which mean "many parts". This is, indeed, an accurate description of the molecules of a polymer, which is made up of a number of identical smaller molecules that are repeatedly linked together to form a long chain.

Polymers can be classified to saturated polymers contain carbon – carbon single bonds and unsaturated polymers contain carbon – carbon double and / or triple bonds.

The difference in the behavior of polymers stems from their molecular structure and shape, molecular size and weight, and amount and type of bond (Covalent or Vander waals bonds). The different chain configurations are shown in Fig. (٢-١) [٦٦-٦٨].

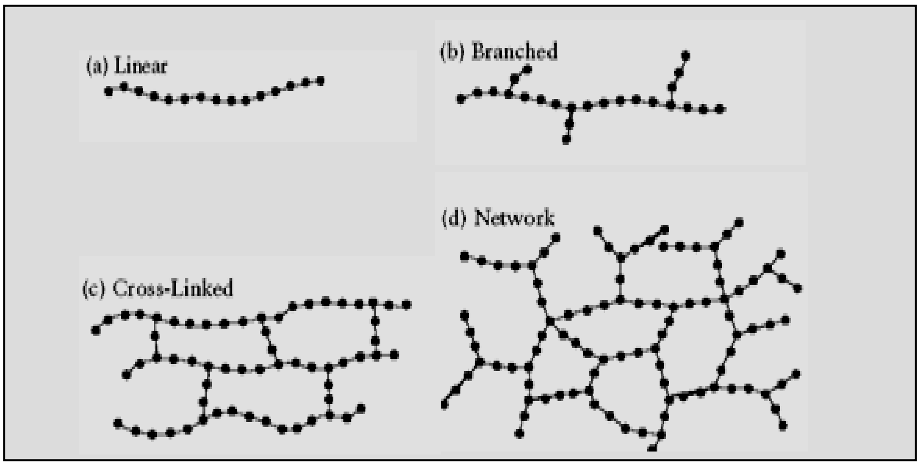


Figure (٢-١): Schematic illustration of polymer chain [١٩].

٢-١-١ Thermoplastics and Thermosets Polymers:

Based on their behavior upon heating – polymers can be divided into two broad categories:-

a- Thermoplastics Polymers :

Thermoplastics generally have linear structures, meaning that their molecules look like linear chains having little breadth but significant length. This type of polymer softens by heating and can then flow viscously to take a desired shape because elevated temperatures tend to decrease the intermolecular coherence of the linear chains. Many thermoplastic polymers are soluble in various solvents.

b- Thermosets Polymers :

The molecules of thermosets usually take the form of a three – dimensional network structure that is mostly cross – linked. Some raw thermosets can take the form of liquids at room temperature. When required, they are converted into solids by curing as a result of heating and / or additives (hardeners). The cured thermosets are insoluble in solvents and soften at high temperature [٧٠-٧٢].

٢-١-٢ Functionality:

The concept of functionality deals with a number of active sites at which chemical reactions can occur. If a monomer has only two possible sites, such as polyethylene or poly(vinyl chloride), it is considered to be bifunctional; if it has three possible sites, it is trifunctional; and so on. Bifunctional monomers tend to form linear polymers, because the presence of two connecting sites promotes the formation of long chains, whereas trifunctional monomers tend to form branched and network (cross – linked) polymeric structures [٧٣,٧٤].

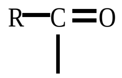
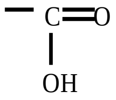
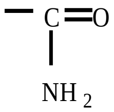
٢-١-٢-١ Reaction of Polymers:

There are some simple reaction of polymers and their use in structural elucidation, such as addition, elimination, substitution and oxidation reaction [٧٥].

٢-١-٢-٢ Functional Groups:

A great variety of other organic compounds may be formed by attachment of atoms or functional groups by replacement of hydrogen or carbon atoms. The most important functional groups are summarized in Table (٢-١) [٧٦].

Table (٢-١): Important functional groups in organic compounds [٧٦].

Group	Name	Resulting Compound
$-OH$	Hydroxyl	Phenols(Aromatics) Alcohols(Aliphatics)
$-O-$	Oxo	Esters
 $R-C=O$	Carbonyl	Aldehydes Ketones,Quinones
 $-C(=O)-OH$	Carboxyl	Carboxylic Acid
$-NH_2$	Amino	Amines
 $-C(=O)-NH_2$	Amido	Amides
$-SH$	Thio	Thiols

٢-١-٢-٣ Typical Primary-Bond Distances and Energies:

From the studies of the positions of atoms in molecules and the energetic of molecular formation and dissociation, it is possible to assign typical energies and lengths to primary bonds. Table (٢-٢) lists some of these properties of interest in polymeric systems [٧٧,٧٨] .

Table (٢-٢): Typical primary-Bond Energies [٧٨]

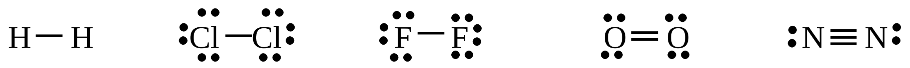
(Acid -Base Interaction)

Bond Type	Bond Energy (KJ/mole)
Primary bonds Ionic	٦٠٠ -١١٠٠
Covalent	٦٠ -٧٠٠
Metallic	١١٠ -٣٥٠
Donor -acceptor bonds	
Bronsted acid -base interactions	Up to ١٠٠٠
Lewis acid -base interaction	Up to ٨٠
Secondary bonds	
Hydrogen bonds Involving fluorine	Up to ٤٠
excluding fluorine	١٠ -٢٥
Van derWaalsbonds	
Permanent dipole –dipole interactions	٤ -٢٠
Dipole -induced dipole interactions	< ٢
Dispersion(London) forces	٠.٠٨ -٤٠

٢-١-٣ Polarity:

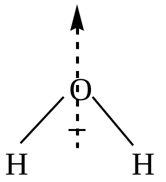
The two atoms involved in covalent bonding do share electrons; often the electrons are not shared equally between them. The key to understanding bond polarity involves the concept of electronegativity of atoms. The net electron affinity that the nucleus of each atom has four electrons is called electronegativity. Two major factors govern electronegativity: the charge of the nucleus and the distance of outer – shell electrons from the nucleus. The larger charge, the greater the atoms affinity for electrons, the farther the outer-shell electrons from the nucleus, the less the atoms affinity for those electrons.

Covalent bonds may be classified into two major categories: non polar and polar. A covalent bond is said to be non polar when the bonding electrons are shared equally between the two atoms involved. For example, the following molecules are non polar:

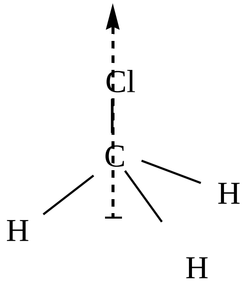


Dipole moment(μ) = 0

A covalent bond is said to be polar when the bonding electrons are shared unequally between the atoms involved. The more electronegative element attracts electrons more strongly and, as a result, has the higher concentration of negative charge about it. The following molecules are polar [٧٩,٨٠].



μ=1.83D



μ =1.87D

٢-٢ Additives:

There are a broad range of additives for polymers; some of the more important additives include plasticizers, lubricants, anti-aging additives, colorants, flame retardants, blowing agents, cross-linking agents, UV protectants, and fillers.

The term additive may be applied to any substance that is incorporated, generally in small concentrations (there are exceptions), in plastic compounds to alter the properties of the resin, the ultimate purpose being either to facilitate processing or to change physical, chemical properties of end products[٨,٨١].

٢-٢-١ Requirements:

It would be desirable if any additive would have no influence on the other properties of compound exceptional the only one which should be varied by a specific additive. It must not cause any unwanted discoloration with white or natural – colored products. It should not cause bad smells and must not be toxic when used for article suitable for contact with foodstuffs [٨٢].

٢-٢-٢ Stabilizers:

Stabilizers and antioxidants are of major importance to the polymer industry because they extend the polymers useful temperature range and service life. Two major areas of polymer deterioration protection are of concern. In the manufacture of synthetic polymers deterioration protection is needed during processing and storage, and in finished polymer products, protection against oxidative deterioration is needed to maintain their original properties. In many cases the stabilizer for the raw polymer also serves as an antioxidant, which is defined as a substance that opposes oxidation or inhibits reactions promoted by oxygen or peroxides. Thus, when used in polymer compositions they may be classified as thermal stabilizers, antioxidants, and UV light stabilizers [٨٣].

Anti-aging additives are incorporated to improve the resistance of the formulation. Examples of aging include attack by oxygen, ozone, dehydrochlorination, and UV degradation. Antioxidants are added to the polymer to stop the free radical reactions that occur during oxidation, these include mercaptans, sulfonic acids, and zinc dialkylthiophosphate.

The absorption of ultraviolet light by a polymer may lead to the production of free radicals. One way to accomplish UV stabilization is by the addition of UV absorbers such as benzophenones, salicylates, and carbon black. They act to dissipate the energy in a harmless fashion. Quenching agents react with the activated polymer molecule. Nickel chelates and hindered amines can be used as quenching agents. Peroxide decomposers may be used to aid in UV stability. In this case, flame retarders may be added, phosphates are an important class of flame retarders. Tritolyl phosphate and trixylyl phosphate are often used in PVC. Halogenated compounds such as chlorinated paraffins may also be used. Antimony oxide is often used in conjunction to obtain better results. Other flame retarders include titanium dioxide, zinc oxide, zinc borate, and red phosphorus. Table (٢-٣) represent the recommodation for the use of antioxidants, and Table (٢-٤) gives the most frequent systems for PVC [٨١,٨٤].

- Stabilizers Effect:

It is the task of stabilizers and antioxidants to protect the polymer material in various ways depending on the degree of energy acting on the material.

١- Absorption: by the stabilizer the incident radiation energy is absorbed and is changed into harmless thermal energy.

٢- Addition: when parts of the polymer molecules are already separated, the stabilizer is to saturate free valences to avoid the addition of oxygen in the free places. The crack – products must also be neutralized.

٣- Bridge formation: when the decomposition proceeds and when the molecular chains are already blown up, the stabilizer is to saturate the free valencies by bridge formation between the parts of the molecule see Fig. (٢-٢) [٨٥].

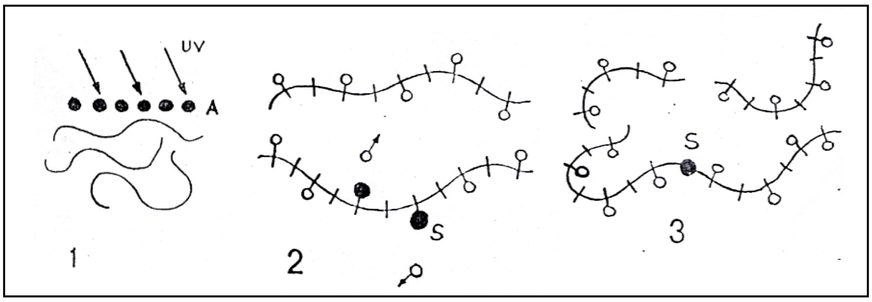


Figure (٢-٢): Effects of stabilization:

١-Absorption ٢-Addition ٣-Bridge formation [٨٠].

٢-٢-٣ Fillers:

Fillers are relatively inert materials that are added to some polymers in amounts ranging from ٥ to ٦٠ percent to improve hardness, abration resistance, impact strength, solvent resistance and to modify electrical characteristics.Some are added to polymers primarily to lower cost. In same respects reinforcements may be regarded as fillers, but they are added mainly to improve the tensile and flexural strength properties of the polymeric material. Most are in fibrous form, Table (٢-٥) shows the fillers and their forms [١,٨١].

Table (٢-٣) :Recommodation for the use of Antioxydants [٨٤].

Polymers	***Antioxidants***
	Shelf aging
Rubber	Diarylamines
	Alkylated diarylamines
	Light aging
Rubber	Derivatives or homologs of hydroquinones.
	Substituted phenols.
	Disbstituted eresols.
	Disubstituted phenols.
	Bisphenols.
	Bisthiophenols.
	Derivatives of eatechol.
	Derivatives of naphthol.
	Alkylated diphenylamines.
Polyethylene (PE)	Carbon black.
	Substituted benzophenones.
	Imidazoles
	Salieylate derivatives.
Polypropylene (PP)	Alkylated phenols plus dilauryl.
	Thiodipropionate.
	Substituted benzophenones.
Polyvinyl chloride (PVC)	Disodium phosphate.
	Organic phosphates, i.e, triphenyl Phosphate, triisooctyl Phosphate.
	Phenolic types.
	Substituted acrylonitriles.
Polyvinyl acetate (PVA)	Substituted Phenols.
	Aromatic amines.
	Organic phosphates.
	Benzoates.
	Heat aging
Rubber	Ketone – amine resins.
PE	Substituted Phenols.
	Aromatic amines.
	Thioether derivatives.
	Carbon black.
PP	Alkylated phenols in canjunction with sulfur compounds, i.e., dilauryl thiodipropionate.
	Dithioeartamates.
PVC	Substituted Phenols.
	Bisphenols.
	Organic phosphates.
PVA	Substituted Phenols.
	Phosphate esters.
	Aromatic amines.

Table (٢-٤) Stabilizers for PVC[٨٤].

Metallic Compounds	Lead	Lead carbonate Tribasic sulfate Dibasic leadphosphide Dibasic Leadphtyhalate Dibasic Leadstearate
	١. calcium- tin ٢. zinc - tin ٣. cadmium - tin ٤. barium – tin	Predominantly stearates and esters of other organic acids Synergistic systems Dibutyltindilaurate Dibutyltinmercaptide
Nitrous compounds	Urea and thiourea compounds Phenylindole, ester of aminocrotonic acid	
Phosphotic compounds	Acrylophosphates	
Sulphuric compounds	Phenolic derivatives	
Epoxides	Mostly secondary stabilizers : high molecular Low molecular	
UV - absorber	Salicylic acid derivatives, benzophenonederivatives, hydroxyphenylobenztriazoles, carbon black	

Table (٢-٥): Forms of various fillers[٦].

Spherical	***Lamellar***	***Fibrous***
Sand / quartz / powder	Mica	Glass fibers
Silica	Talc	Asbestos
Glass spheres	Graphite	Wollastonite
Calcium carbonate	Kaolin	Carbon fibers
Carbon black		Whiskers
Metallic oxides		Cellulose
		Synthetic fibers

٢-٢-٤ Plasticizers:

A plasticizer has been defined as a material incorporated in a plastic to increase its workability and its flexibility. The addition of the plasticizer may lower the glass transition temperature and the elastic modulus of the plastic Fig. (٢-٣), improve impact resistance of the final product and lowers the melt viscosity.

Plasticizers are usually in form of high-viscosity liquids. The plasticizers should be capable of withstanding the high processing temperatures without degradation and discoloration that would adversely affect the end product. The plasticizer should be withstanding any environmental condition that the final product will see. This might include UV exposure, fungal attack, or water. In addition, it is important that the plasticizer show low volatively and migration so that the properties of the plasticized polymers will remain relatively stable over time [١].

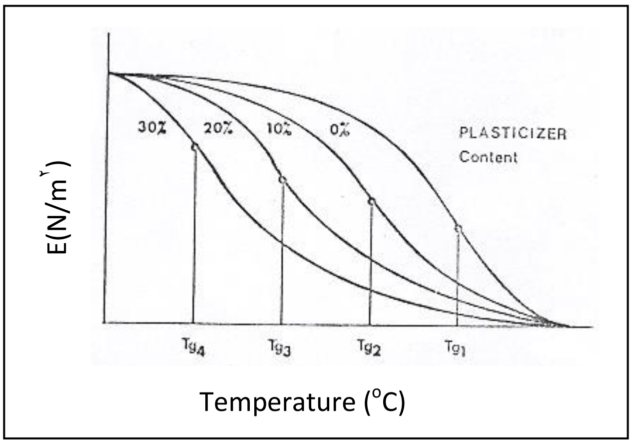


Figure (٢-٣): Effect of plasticizing [٨٢].

Plasticizers are medium molecular weight, relatively high - boiling, colourless liquids, normally non-polymeric. They are added in amounts which are around ٥٠ percent. The following types of plasticizer are in common use:

a- Phthalate esters, accounting for over half of the total volume of plasticizers used. Di (٢ – ethylhexyl) phthalate (dioctyl phathalate, DOP) is the dominant plasticizer for PVC.

b- Phosphate esters, chiefly tricresyl phosphate, valued primarily for their flame proofing characteristics.

c- Adipates, azelates, oleates, and sebacates, used chiefly in vinyl resins for improving low-temperature flexibility.

d- Epoxy plasticizers, produced by reacting hydrogen peroxide with unsaturated vegetable oils and fatty acids.

e- Fatty acid esters from natural sources, used primarily as extenders to reduce cost (secondary plasticizers).

f- Glycol derivatives, employed mainly as lubricants and mold – release agents, and as plasticizers for poly (vinyl alcohol).

g- Sulfonamides, used to plasticized cellulose esters, phenolic and amino resins, and amide and protein plastics.

h- Hydrocarbons and hydrocarbon derivatives, serving as secondary plasticizers [٨١,٨٤]

٢-٢-٤-١ Mechanism of plasticizing:

Two theories have been proposed to account for the major observable effects: the lubricity and the gel theories. These materials function by increasing the distance between adjacent chains and reducing the effects of intermolecular forces and the tendency toward crystallization, thereby facilitating the relative mobility of the polymer molecule Fig. (٢-٤)[٨٥].

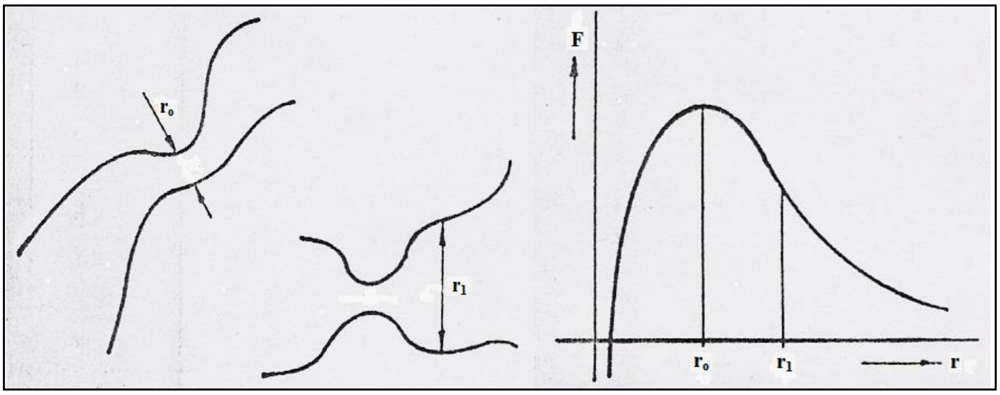


Figure (٢-٤): Mechanism of plasticizing [٨٢].

٢-٢-٥ Colorants:

Colorants are fine distributed particles which are either pigments or dyes. Colorants absorb complementary color of the desired color from incident white light.

Each incident intensity ($I_{٠}$) is divided in a reflectance (I_R), absorbance (I_A) and transmittance (I_T) component Fig (٢-٥). Absorption by chemical resonance of colorant molecules causes the effect of color in reflexion and/or transmission [٨٥].

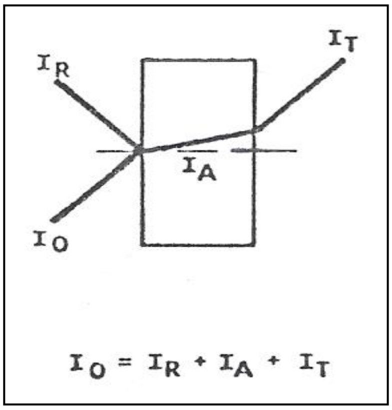


Figure (٢-٥): Optical Behavior of Colorants [٨٢].

Properties which are common to pigments and dyes include thermal stability, light fastness, weathering resistance, migration, and influence on rheological properties of plastic melts. Most organic pigments have chemical structures that are closely related to dyes, and some dyes become pigments after application (vat dyes).

Thermal stability depends on both temperature and time. Light might also cause degradation of colorants, and hence methods have been developed for testing fastness to natural day light or to artificial light. Weathering resistance is of special relevance for plastic materials made for outdoor use, where UV radiation, oxygen, temperature, moisture, and atmospheric contaminants contribute to the degradation of the colorant. In addition, degradation is affected by the type of polymer and by includes.

Migration is a technical term with some what different meaning on whether it used for describing the transfer of substances to foodstuffs or the movement of colorants within plastic materials. Pigments and dyes may also increase the viscosity of plastic melts. This effect depends highly on the amount added and is more significant for pigments than for dyes .Tables (٢-٦) and (٢-٧) show some of inorganic and organic pigments respectively [٨٦].

Table (٢-٦) :Some of the inorganic pigments [٨٦].

Pigments	*Chemical Structure*
White	Titanium dioxide $TiO_٢$
Black	Carbon black C
Red	Iron oxide $Fe_٢O_٣$
Yellow	Titanium / nickel / antimony oxide
Green	Cobalt / titanium / nickel / zinc oxide
Blue	Cobalt / titanium / chrome oxide
Brown	Chrome / antimony / titanium oxide

Table (٢-٧) :Some of the organic pigments [٨٦].

Pigments	***Chemical Structure***
Orange	٤ – chloro – ٢ - nitroaniline
Red	β – oxynaphthoic acid
Yellow	٢ – methoxyaniline
Green	Phthalocyanine
Violet	Quinacridone
Blue	Anthraquinona
Black	Monoazo

٢-٢-٥-١ Regulations:

- *The performances of the pigment will depend on:*

١- Chemical structures.

٢-The surface properties.

٣-The crystallinity.

٤-Particle size and size distribution.

Pigments often interfere with the crystallization process during molding, leading to dimensional stability problems like distortion called warpage.

Some pigments may accelerate crystallization of the polymer which can strongly influence the morphology and thus the mechanical properties of the molded article. This effect is obviously very much enhanced if the rigidity of the item is particularly weak (thin wall pieces, no internal reinforcements). To counter that mold design, there is a key role to play.

- *Effect of colorant defect on polymer properties:*

a) Dispersion:

Dispersion means the degree to which pigment agglomerates are broken down into primary particles and aggregates. The more finely the pigment is dispersed (smaller average particle size), the larger the total surface area of the pigment particles and the greater its color strength is see Fig. (٢-٦).

The shade and the opacity of the colored material are also affected by the particle size distribution of the dispersed pigment. As a general rule to disperse agglomerates of transparent organic pigments higher shear forces are needed than when dispersing agglomerates of opaque organic pigments.

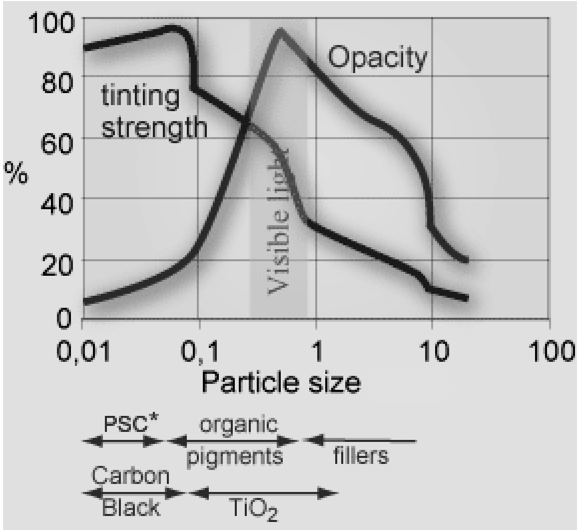


Figure (٢-٦): Effect of particle size on opacity tinting strength [٨٧].

b) Concentration:

Resistance properties in plastics are dependent on pigment concentration, and the polymer system being used. Regarding pigment performance, if a pigment is applied at a level lower than "Critical Concentration", then it is likely that the performance of the colorant will be dramatically reduced.

c) Migration:

If a colorant partially dissolves in the plastic, there is a possibility; it will migrate to the surface or into materials in contact with the plastic. The term migration is used to describe this bleeding and blooming behavior of the colorant. Three types of migration can be observed:

-Solvent Bleeding – the release of colorant from the colored plastic into a solvent.

-Contact Bleeding – the colorant migrates from the colored plastic object into another object see Fig. (٢-٧).

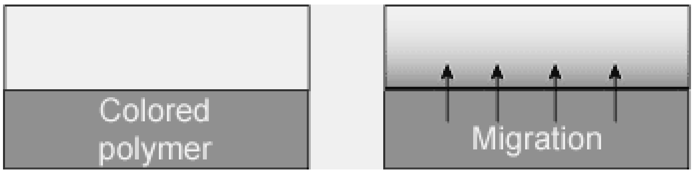


Figure (٢-٧): Illustration of contact bleeding [٨٧].

-Blooming – this is a very slow process where the pigment migrates to the surface of the plastic resulting in a hazy surface which often has a bronze like appearance see Fig. (٢-٨)[٨٨-٩٠].

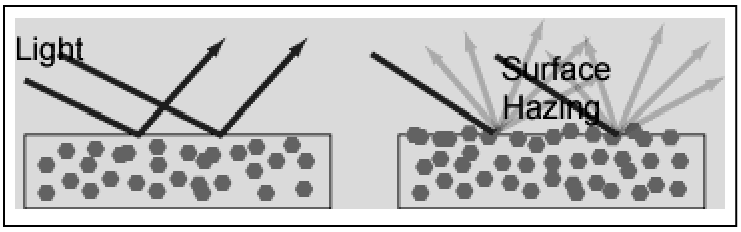


Figure (٢-٨): Illustration of blooming effect [٨٧].

٢-٢-٥-٢ Pigments:

Pigments are colorants that are "insoluble" in the medium in which they are used. They exhibit no affinity for materials upon which they are applied Pigments are particles, usually with a size in the ٠.٠١ – ١ µm range. The particle size is one of several parameters of technical importance for the pigment products.

They differ from dyes in that they can be either transparent or opaque (dyes are only transparent) and selectively absorb and scatter light Fig. (٢-٥). As a type of colorant, pigments can be closed as either organic or inorganic, natural or synthetic [٨٢].

٢-٢-٥-٣ Dyes:

Dyes are colorants, which are easily soluble in the medium in which they are used. They may either be organic or inorganic. Their technical application with plastics is not too favourable Fig. (٢-٩)[٧].

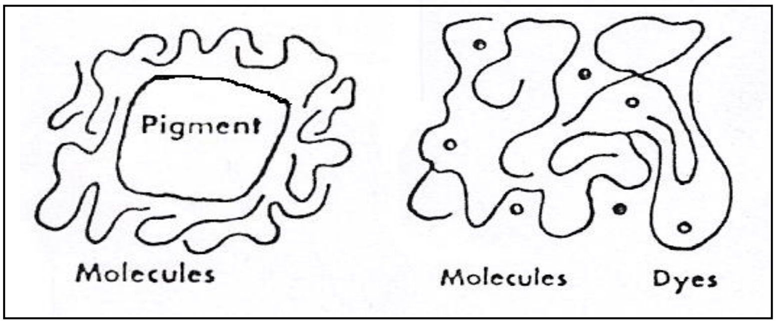


Figure (٢-٩): Mechanism of coloration [٨٢].

٢-٢-٦ Major Hazards of Synthetic Additives:

Bioaccumulation means that a substance is fat-soluble and therefore it is built up in the tissues of living things. Most bioaccumulative substances, including many formed during the plastics lifecycle, magnify as they move up the food chain, reaching concentrations in species high on the food chain that are millions of times greater than their levels in the ambient environment. These substances also cross the placenta easily and concentrate in the breast milk of human and other mammals.

The feedstock's, additives, and by-products produced and released during the lifecycle of plastics have been shown to cause a range of health hazards, in some cases at extremely low doses, including:

· Cancer.

· Disruption of the endocrine system.

· Reproductive impairment.

· Impaired child development and birth defects.

· Neurotoxicity (damage to the brain or its function), and

· Immune system suppression.

- *Dioxin poses health risks to the general public that are already too high*: The dioxin “body burden" of the general human population of the United States is already in the range at which adverse health impacts occur in laboratory animals. The dioxin exposure of the average American already poses a calculated cancer risk of one in ١٠٠٠ to one in ١٠٠ - thousands of times greater than the usual standard for an “acceptable risk”.

-*Phthalate plasticizers*: In its pure form, some plastics are rigid and brittle. To make flexible plastics products, such as roofing materials, floor tiles and wall coverings, plasticizers must be added to plastics in large quantities - up to ٦٠ percent of the final product by weight. The dominant groups of plasticizers used in plastics such as vinyl are the class of compounds called phthalates, which pose considerable health and environmental hazards.

-*Massive quantities of phthalates are released into the environment each year*: Millions of pounds of phthalates are released annually into the environment during the formulation and molding of vinyl products. Phthalates are also released when vinyl is disposed of in landfills or incinerators or when PVC products burn accidentally.

-*Phthalates leach out of vinyl products*: Phthalates are not chemically bonded to the plastic but are merely mixed with the polymer during formulation. They therefore leach out of the plastic over time into air, water, or other substances with which vinyl comes in contact.

-*Phthalates damage reproduction and development*: Phthalates have been found to damage the reproductive system, causing infertility, testicular damage, reduced sperm count, suppressed ovulation, and abnormal development and function of the testes and male reproductive tract in laboratory animals. They are known carcinogens in laboratory animals [٩١,٩٢].

- *Lead and other heavy metal stabilizers*: Because plastics catalyze its own decomposition, metal stabilizers are added to vinyl for construction and other extended-life applications. Common plastics additives that are particularly hazardous are lead, cadmium, and organotins, with global consumption of each by plastics estimated in the thousands of tons per year.

-*Metals do not degrade in the environment*: All three of the major plastics stabilizers resist environmental breakdown and have become global pollutants.

-*Metal stabilizers are highly toxic*: Lead is an exquisitely potent developmental toxicant, damaging brain development and reducing the cognitive ability and IQ of children in infinitesimal doses. Cadmium is a potent neurotoxin and carcinogen, and organotins can suppress immunity and disrupt the endocrine system.

-*Metal stabilizers are released through out the plastics product lifecycle*: Metal stabilizers are released from plastics products when they are formulated, used, and disposed. Metals cannot be destroyed by incineration but are released entirely into the environment, via air emissions or ash residues. Trash incinerators are the dominant source of lead and cadmium pollution [٩٣].

٢-٣ Polymer Degradation:

Polymer degradation it is the collective name given to various processes which degrade polymers, i.e., deteriorate their properties or ruin their outward appearance.

Macromolecules are composed of monomeric units which are joined by chemical bonds to each other. The monomeric units contain chemical bonds which are either in the main chain of the macromolecule or the connect various atoms or side groups to it. Side groups, if they are presented, they contain additional chemical bonds. All of these bonds may be reaction sites in polymer degradation, and various energy sources may be effective in supplying the energy necessary to break the bonds. The dissociation energies of chemical bonds in common polymers range from about ٣٣٩$kJmol^{-١}$ (C-Cl) to ٤٧٣ $kJmol^{-١}$ (C-F) with (C-C) between ٣٤٧ $kJmol^{-١}$. The most important types of energy that cause polymer degradation are heat, mechanical energy, and radiation. The most common form of radiant energy which causes degradation is that of UV component of sunlight , the energy of a photon with λ=٣٠٠ nm is about ٣٩٧$kJmol^{-١}$, which is higher than most bond dissociation energies in polymers . Generally speaking the factors affecting polymer stability are [٩٤-٩٦]:

- Chemical structure.
- Comonomeric units.
- Tacticity.
- Physical and morphological factors.
- Internal mechanical stresses.
- Contaminants.

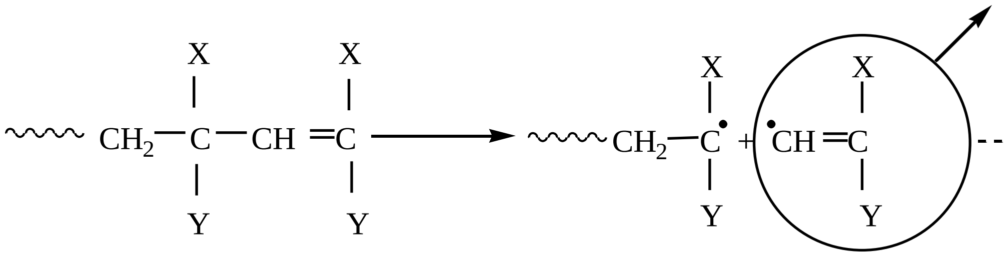
٢-٣-١ Types of polymer Degradation:

There are various schemes to classify polymer degradation. Because of its complexity, with regard to both the causes and the response of the polymer, classification is usually performed on the basis of the dominating features [٩٧].

٢-٣-١-١ Depolymerization:

Depolymerization is essentially a reversal of the polymerization process. In the simplest case, depolymerization consists of initiation at chain ends, depropagation, and termination. In the depropagation step, monomer's is unzipped rapidly from the activated chain ends. The main characteristic of degradation processes with dominating depolymerization character is the high monomer yield.

Depolymerization can be the dominating degradation process of a polymer if initiation by main chain scission is possible, which is a necessary condition of depolymerization because this process produces the terminal active site capable of depropagation. This is usually possible if the chain end itself is a weak of the polymer as in the case of macromolecules with terminal double bond formed by termination with disproporation of the growing radical's formulae (٢-١).



$$\sim\!\sim\; CH_2-\overset{X}{\underset{Y}{C}}-CH=\overset{X}{\underset{Y}{C}} \longrightarrow \sim\!\sim\; CH_2-\overset{X}{\underset{Y}{\dot{C}}} + \dot{C}H=\overset{X}{\underset{Y}{C}}$$

-----(2-1)

The monomer radical formed in this reaction usually volatilizes, but the macro – radical remains in the system as long as its length is higher than the volatilization limit at the degradation temperature [٩٨].

٢-٣-١-٢ Random Chain Scission and Cross – linking:

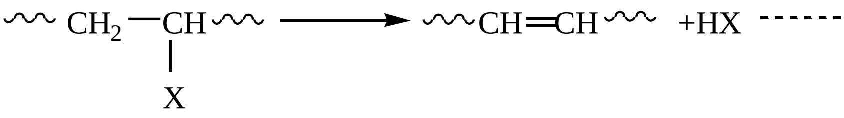
The most common form of polymer deterioration is the random degradation. In macromolecules, the overwhelming majorities of chemical bonds which participate in a specific reaction have practically the same dissociation energy and are statistically equivalent with respect to this reaction. Some degradation processes can only be initiated at the weak sites in the polymer; however, once initiated, the reaction usually proceeds randomly: the active intermediates (e.g., radicals) attack the reactive bonds still present statistically, i.e., without discrimination.

Typical examples for degradation processes with dominating random chain scission character are hydrolysis, high temperature thermal degradation, and degradation by radiation [٩٩].

٢-٣-١-٣ Degradation Without chain Scission:

A very important type of polymer degradation consists of those processes which take place without scission of the main polymer chain; characteristic of this kind of degradation is the participation of side groups in the reaction.

From vinyl polymers of the structure $(-CH_{٢} - CHX-)_{n}$ where x is an electronegative group (e.g. a halogen atom, a hydroxyl or a acetate group), HX elimination is the most common form of degradation formulae (٢-٢).



$$\sim CH_2-\underset{X}{\underset{|}{CH}}\sim \longrightarrow \sim CH{=}CH\sim + HX \text{ ------ } (2\text{-}2)$$

The elimination of side groups from the polymer usually proceeds via a nonradical mechanism [١٠٠,١٠١].

٢-٣-١-٤ Oxidative Degradation:

The reaction of organic compounds initiated by the attack of molecular oxygen is called outoxidation. Peroxides or other oxygenated compounds incorporated into a polymer during its synthesis or processing may increase its susceptibility to oxidation.

Polymer oxidation reactions generally show an induction period during which no visible changes occur in the material. However, after the induction period, the rate of oxidation increases rapidly (autocatalysis): the first formed oxidation products accelerate the further degradation.

The oxidative degradation of polymers is a free radical chain reaction. An important difference from some other chain reactions is that besides the usual three steps: initation, propagation, and termination formulae (٢-٣) [١٠٢].

$$\left\{\begin{array}{lcl} RH+O_2 & \longrightarrow & \overset{\bullet}{R}+HO_{\overset{\bullet}{2}} \\ \overset{\bullet}{R}+O_2 & \longrightarrow & R\overset{\bullet}{O}_2 \\ R\overset{\bullet}{O}_2+RH & \longrightarrow & \overset{\bullet}{R}+RO_2H \\ \overset{\bullet}{R},R\overset{\bullet}{O}_{2,\ldots} & \longrightarrow & \text{products} \end{array}\right\} \text{-----}\!\!\longrightarrow\!\!\!\!- (2\text{-}3)$$

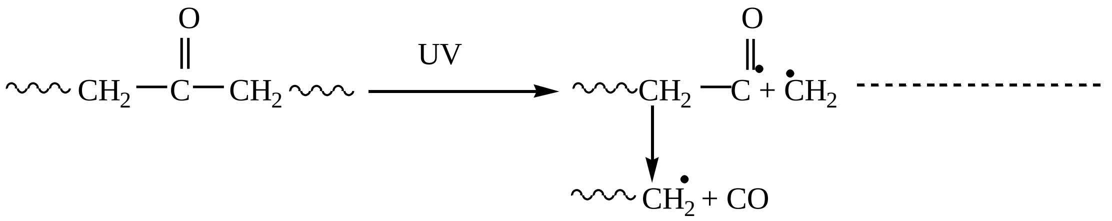
Formulae (٢-٣) simplified general scheme of polymer oxidation [١٠٢].

٢-٣-١-٥ Photodegradation:

Polymers have different photodegradation sensitivities to UV light of different wavelength. The varying sensitivities result from differences in the chemical structure, the maximum sensitivity of several polymers (as determined by the bond dissociation energies) is in the range of ٢٩٠-٤٠٠ nm.

The physical processes involved in photodegradation include absorption of light by the material, electronic excitation of the molecules, and deactivation by radiative or radiationless energy transitions, or by energy transfer to some acceptor, when the life time of the excited state is sufficiently long, the species can participate in various chemical transformations.

The role of carbonyl groups in polymer photooxidation is of great importance because once they have been formed they absorb UV light readily, hence, excitation the singlet and triplet states is easy formulae (٢-٤)[١٠٣,١٠٤].



$$\sim\!\sim CH_2-\overset{\overset{O}{\|}}{C}-CH_2\sim\!\sim \xrightarrow{UV} \sim\!\sim CH_2-\overset{\overset{O}{\|}}{\dot{C}}+\dot{C}H_2 \quad (2\text{-}4)$$

$$\downarrow$$

$$\sim\!\sim \dot{C}H_2 + CO$$

٢-٣-١-٦ Biodegradation:

Biodegradation or biological degradation of polymers consists of those processes which are resulted from an attack on the material by living organisms, e.g., bacteria, fungi, insects, and rodents. Biodegradation is fundamentally a chemical process involving enzymes produced by microorganisms. High humidity, moderately increased temperature, and darkness are usually favorable for proper functioning of microorganisms [١٠٠,١٠٥].

٢-٣-١-٧ Mechanical Degradation:

Mechanical degradation of a polymer includes, in a broad sense, every kind of mechanically induced breakdown of the material. Thus, irreversible deformation, crazing, cracking, fracture, and fatigue of polymeric bodies under static or dynamic loading are processes which lead to mechanical deterioration.

The term mechanochemistry covers a broader field: it deals with those processes which utilize stress – induced chemical changes to transform polymers

into new materials (e.g., synthesis of block and graft copolymers) [١٠٦].

٢-٤ Radiation and Other Weather Factors:

The process of weathering, however, encompasses the action of elements in addition to radiation, and the Combination of factors produced an effect greater than the sum of the individual effect. Degradation due to radiation is accelerated when the other elements operate at the same time.

٢-٤-١ Radiation and Water:

Fortunately, two elements of weather, radiation and water, tend to operate at different times. Materials can be irradiated, however, after having been wet by rain or when they have high moisture content from overnight high humidity. Time of wetness, therefore, is an important parameter in relating climatic conditions to exterior degradation. The action of the combined elements can follow several paths, with radiation accelerating the effect of water or the converse.

Most organic materials are resistant to attack by water at normal temperatures. It is possible, however, for radiation to raise the temperature to the point where solution or hydrolysis can occur. Thus, plasticizers for vinyl coating and plastics may be removed if they are appreciably soluble in water at elevated temperatures. Strength of polyester laminates can also be reduced through attack by water either on the resin itself or on the bond between the resin and the glass fiber [١٠٧].

٢-٤-٢ Radiation and Oxygen:

A natural weathering combination that has probably often greater effect is oxygen and radiation, referred to technically as photo-oxidation. Materials subjected to oxygen are degraded much faster in the presence of radiation than in its absence and vise versa. For example, discoloration of polystyrene occurs more rapidly when irradiation takes place in air or oxygen, as shown in Table (٢-٨). Also, the oxygen content of the product is about ten times greater when both elements operate together. It has been demonstrated that rubber can absorb ٥ percent oxygen in the dark without major changes, but when rubber containing only ٢ percent oxygen was irradiated the elongation at break decreased from ١١٠٠ to ١٠percent. In a third case, the light from a ١٥٠-watt bulb accelerated the absorption of oxygen by natural rubber. With saturated polymers there is little damage from oxygen at room temperature if UV is absent [١٠٧].

Table (٢-٨): Photo - oxidation of polystyrene [١٠٧].

Oxygen pressure mm	***UV radiation time hr***	***Oxygen in product %***	***color***
٠	٠	٠.١١	nearly color less
٠	٢٥٠	٠.١٣	Light yellow
٢٠	٠	٠.١٠	Nearly color less
٢٠	٢٥٠	٠.١٤	Yellow-orange

*Note: total exposure time ٢٥٠ hours at ١١٥-١٢٠ºC in all cases.

٢-٤-٣ Radiation and Heat:

The radiation referred to in this combination is again ultraviolet, infrared radiation is converted to heat. Degradation reactions that proceed only at temperatures higher than those reached on natural exposure may occur at much lower temperatures under the influence of UV. Thus, polystyrene heated in a vacuum remains colorless as it depolymerizes at ٣٢٠ºC. Pre-irradiated polystyrene rapidly turns yellow, then brown, and finally black at considerably lower temperature. Poly (vinyl chloride) also is degraded faster thermally after or during irradiation. Plastics that have been held at high temperatures too long during molding are more susceptible to UV degradation upon exposure.

Finally, there is the combination of the three elements: heat, radiation and oxygen. As expected, together they are more damaging than any combination of only two of the factor. This is illustrated in Table (٢-٩) [١٠٧].

Table (٢-٩): Degradation of polyvinyl chloride [١٠٧].

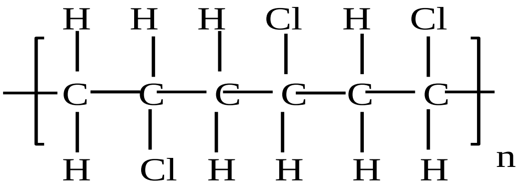
Exposure Condition		***Atmosphere***	
Radiation	***Heat***	***Nitrogen***	***Oxygen***
None	١ hr , ١٥٠°C	٠.٠٠٣٥	٠.٠٠٤٣
Sun. Lamp	١hr , ١٥٠°C	٠.٠٠٩	٠.٠٢١

Note: Measured by amount of HCl produced.

٢-٥ Polymers Used:

٢-٥-١ Poly Vinyl Chloride (PVC):

PVC is a thermoplastic polymer. It is essentially just the polyethylene molecule with some of its hydrogen atoms replaced by chlorine atoms to give a knobbly structure it's for the molecule. The PVC has a linear chain with largely atactic Fig. (٢-١٠).



$$-\left[\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}\right]_n-$$

Figure (٢-١٠): PVC structure [١٠٨].

The PVC family consists of two contrasting types of material, the rigid (unplasticized polymer UPVC) and plasticize PVC.

Because of lower prices, widely mechanical properties range and can be modified this properties by additives the PVC dominate the market. But the PVC embrittlement of the surface as a result of photo – oxidation is a major cause of fracture problems in polymers. The photons that make up the ultraviolet component of sunlight have enough energy to split chemical bonds and thus set off a chain reaction in which the surface layer becomes slowly oxidized. This brittle surface layer readily form cracks at low strains which can propagate into and through the unaffected material below, Table (٢-١٠) shows mechanical and thermal properties.

UPVC products include house siding, extruded pipe, and thermoformed and injection molded parts. UPVC is calendared into credit cards. Plasticized PVC is used in applications such as flexible tubing, floor mats, garden house, shrink wrap, insulating coatings on wires, and bottles [١٠٨-١١٠].

Table (٢-١٠): Polymers properties [٦٨,٦٩,١٠٩].

properties	***UPVC***	***ER***	***UPE***
Density g/cm^{٣}	١.٣٨	١.١٥-١.٣	١.١-١.٣
Tensile strength MPa	٥٠-٦٠	٣٥-١٤٠	٥٥
E – modulus GPa	٢-٣	٣.٥-١٧	٢.٤-١٧
Impact strength kJ/m^{٢} ×١٠$^{-٥}$	٣	١.٧-٥.٨	٠.٦-١٣.٧
Elongation %	٢-٤٠	٣-٦	٥
Flexural strength ١٠^{٤} Pa		١-١.٨	٠.٨
Max. temperature °C	٨٠-١٠٤	٢٣٠-٢٦٠	١٢٠-١٨٠

٢-٥-٢ Epoxy Resins (ER):

Epoxy resins are a family of thermoset polymers of increasing importance in engineering. These polymers become highly cross – linked by reaction with hardeners and got their name from the epoxide group at the ends of the molecular chains. Epoxy resins preparation from epichlorohydrine and bisphenol – A see Fig. (٢-١١).

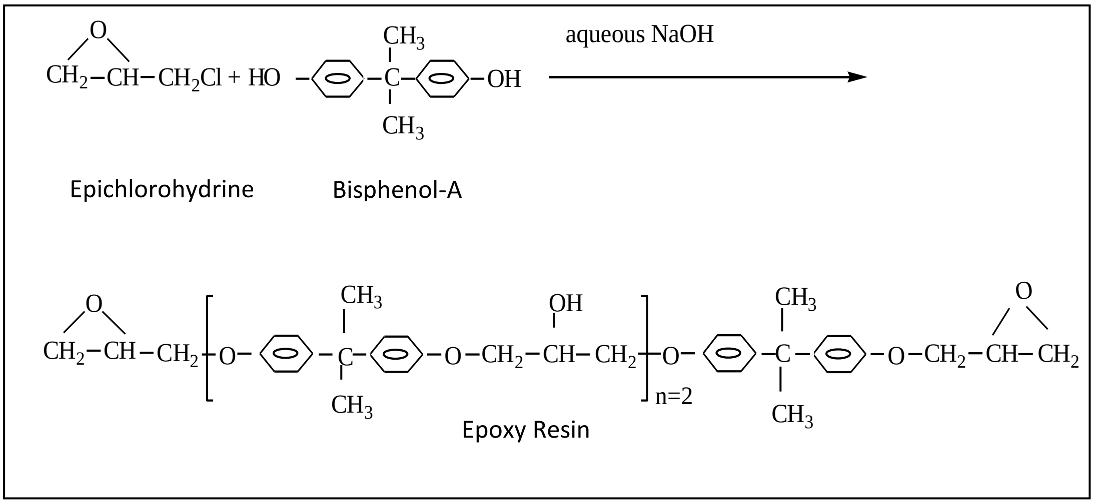


Figure (٢-١١): Schematic Epoxy resins preparation [٧٨].

The most common cross – linking agents for epoxies are the amines and curing reaction Fig. (٢-١٢)[٧٨,١٠٨,١١١].

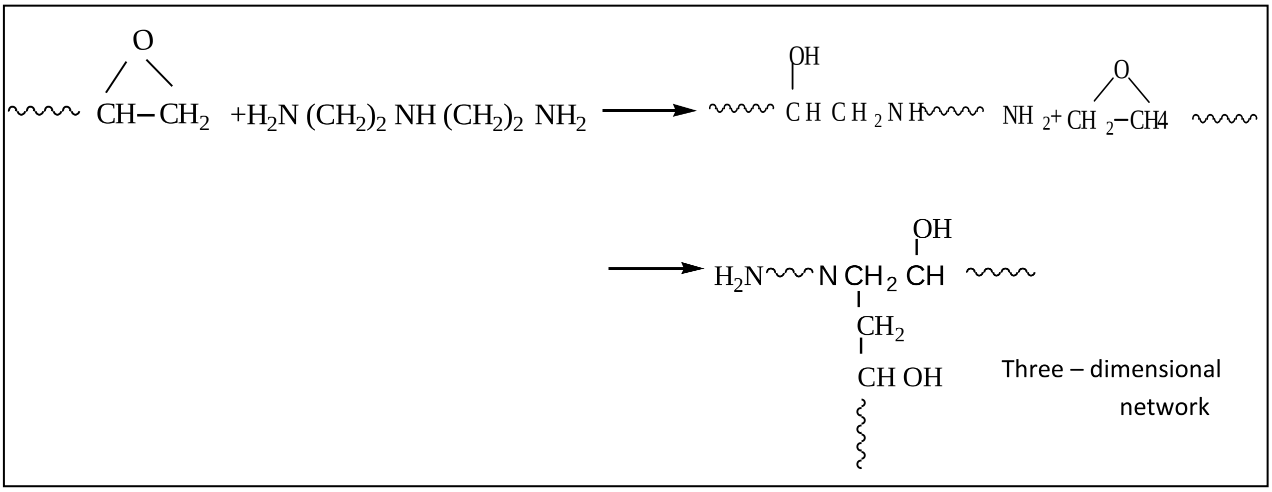


Figure (٢-١٢): Schematic representation of an epoxy cross – linking [٧٨].

They are glass at room temperature and have a good temperature resistance, stability of dimensions upon curing (below ٠.٣٪) and a very high fluidity. The main properties are listed in Table (٢-١٠).

The common application of epoxy resins is as adhesives with the addition of fibers and reinforcements and laminates, protective coatings for cars, drums and wires, encapsulation of transistors and other electrical components…. [١١٢].

٢-٥-٣ Unsaturated Polyesters (UPE):

UPE consist of unsaturated material maleic anhydride and ethylene glycol there are dissolved in a reactive monomer (styrene), when catalyst is added (Methyl Ethyl Ktone Peroxide MEKP) and accelerator (Cobalt Naphanate) the double bonds open and an addition reaction leads to the formation of a highly cross – linked network Fig. (٢-١٣).

The term GRP usually refers to glass – reinforced polyester, which are characterized by high stiffness, strength and toughness, resistance to chemical attack and dimensional stability. Major applications include building and construction, ship and boat hulls, chemical plant, and various forms of transport. The main properties are listed in Table (٢-١٠) [١,١٠٩,١١٣].

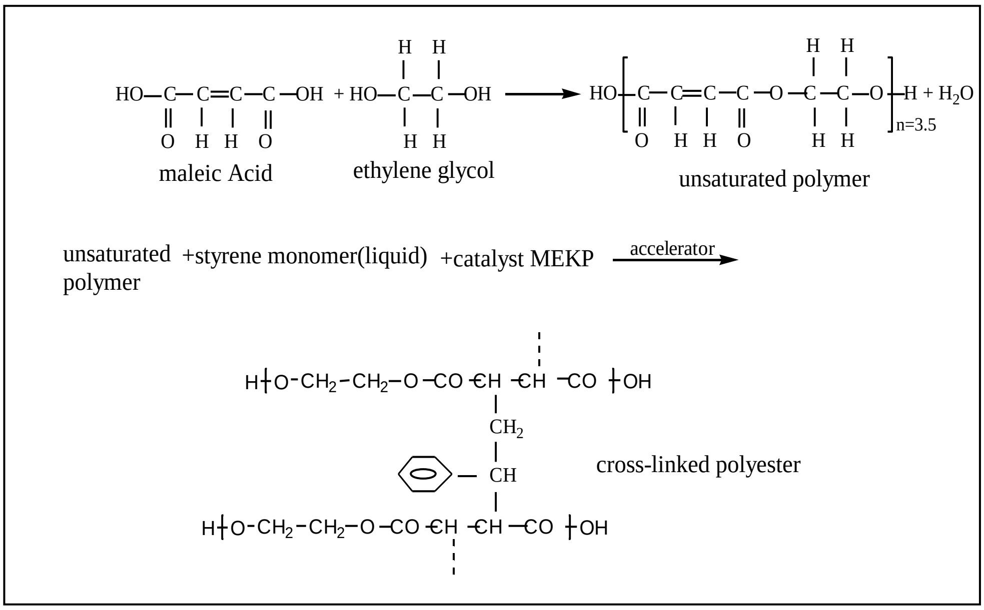


Figure (٢-١٣): Illustrates the nature of the polymer resin and curative molecules during the Curing sequence [١١٣].

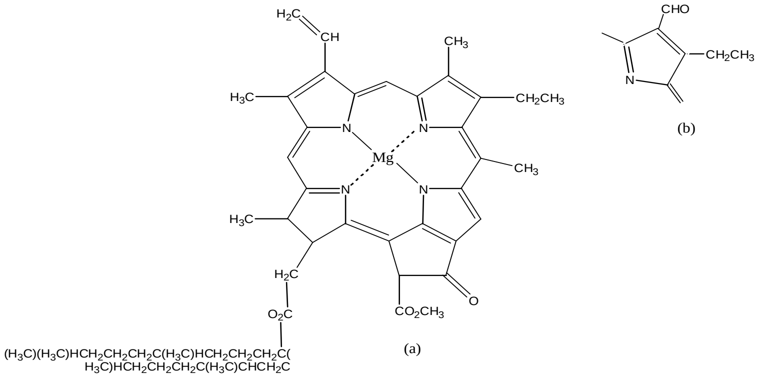
٢-٦ Natural Pigments Used:

A pigment is a substance that absorbs light at specific wave lengths. There are many different pigments in plant parts, such as, chlorophyll, carotenids and anthocyanins. Most are relatively large molecules with hydrocarbon skeletons [١١٤].

٢-٦-١ Chlorophylls:

The chlorophylls are the essential catalysts of photosynthesis and occur universally as green pigments in all photosynthetic plant tissues. They occur in the chloroplasts in relatively large amounts, often bound to protein but are readily extracted into lipid solvents such as, acetone or ether.

Chemically, each of them contains a porphyrin (tetrapyrrole) nucleus with a chelated magnesium atom in the centre and a long – chain hydrocarbon (phytyl) side chain attached through a carboxylic acid group. There are at least five types' chlorophylls in plants, all with the same basic structure but which show variations in the nature of the aliphatic side chains attached to the porphyrin nucleus, Fig. (٢-١٤). Thus, the structure of chlorophyll b only differs from that of an in having an aldehyde group instead of a methyl substituent attached to the top right – hand pyrrole ring. Chlorophylls a and b occur in higher plants, ferns and mosses; chlorophylls c to e are only found in algae, while yet other chlorophylls are confined specifically to certain bacteria [١١٥].



$C_{53}H_{70}MgN_4O_3$
Exact Mass: 834.53
Mol. Wt.: 835.45
C, 76.19; H, 8.45; Mg, 2.91; N, 6.71; O, 5.75 (percent)

Figure (٢-١٤): The structures of chlorophyll a and b[٧].

This highly unsaturated molecule contains many conjugated double bonds and would be expected to absorb light in the visible as well as in the UV portion of the electromagnetic spectrum.

The chlorophylls are readily differentiated by their relatively complex UV and visible absorption curves. They show major peaks at about ٤٠٠nm, a number of minor peaks, between ٥٠٠ and ٦٠٠nm, and a major peak above ٦٢٥nm, Fig. (٢-١٥) [٧,١١٦,١١٧].

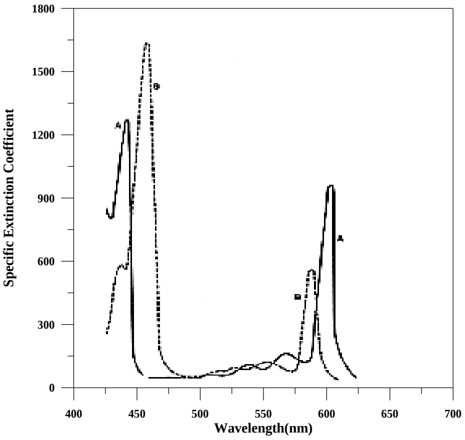


Figure (٢-١٥): Absorption spectra of A-*chlorophyll a* B-*chlorophyll b*[٧].

٢-٦-٢ Carotenoids:

Carotenoids, which are $C_{٤٠}$ tetraterpenoids, are an extremely widely distributed group of lipid – soluble pigments, found in all kinds of plants from simple bacteria to yellow – flowered composites. Most carotenoids occur in green leaves, where the abundand chlorophyll there masks them.

Although there are now over ٣٠٠ known cartenoids, β - carotene and xanthophylls are common on higher plants, Fig. (٢-١٦).

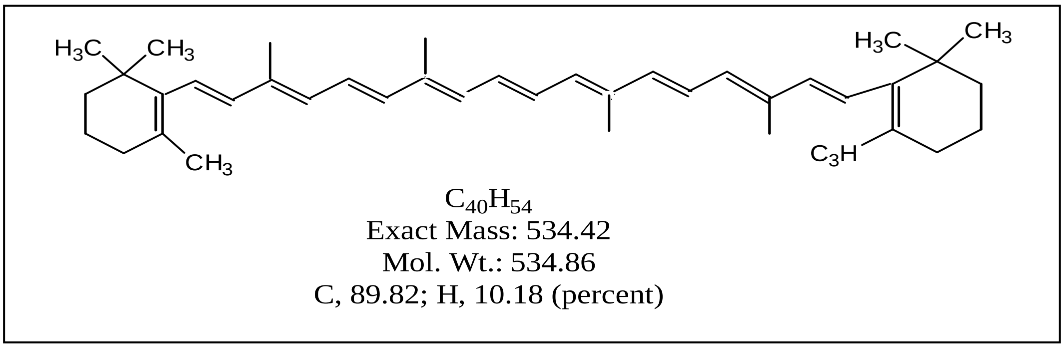


Figure (٢-١٦): The structures of β - *carotene* [١١٣].

Those pigments have an accessory light harvesting and absorb at wave lengths in between the maxima of the chlorophylls. The spectra of carotenoids are quite characteristic between ٤٣٠ and ٥٤٠nm, with a major peak around ٤٥٠nm usually two minor peaks either side, Fig. (٢-١٧) [١١٨,١١٩].

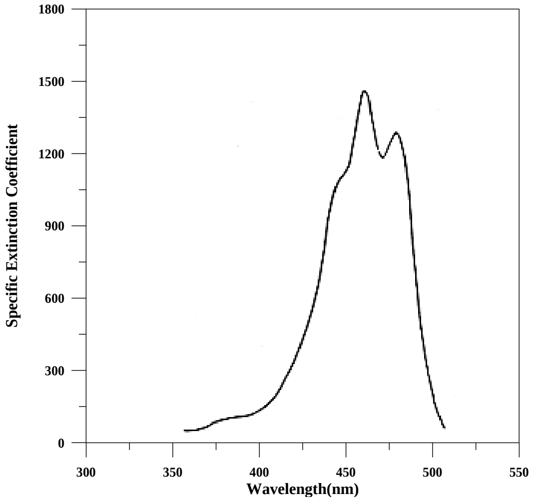
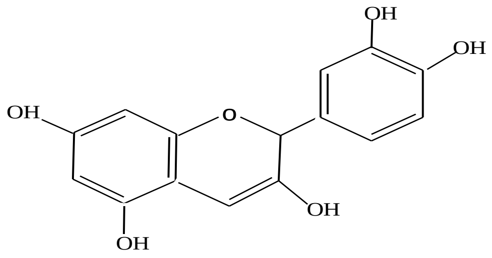


Figure (٢-١٧): Visible spectrum of β- carotene [٩٠].

٣-٦-٣ Anthocyanins:

The anthocyanins are the most important and widespread group of coloring matters in plants. This intensely colored water – soluble pigments are responsible for nearly all the pink, scarlet, red, mauve, violet and blue colors in the petals, leaves and fruits of higher plants. The anthocyanins are all based chemically on the aromatic structure consisting of a double ring attached by a single bond to a third ring; Fig. (٢-١٨).



$C_{27}H_{55}O_5$
Exact Mass: 459.40
Mol. Wt.: 459.72
C, 70.54; H, 12.06; O, 17.40 (percent)

Figure (٢-١٨): The structures of anthocyanins [١٢٠].

In leaves they block for ultraviolet (UV) light (which is highly destructive to nucleic acids and proteins), while selectively admitting light of blue and red wavelengths which is crucial for photosynthesis. The spectra of anthocyanins are characteristic between ٤٧٥ and ٥٥٠ nm; see Fig. (٢-١٩) [٩٠,١٢٠].

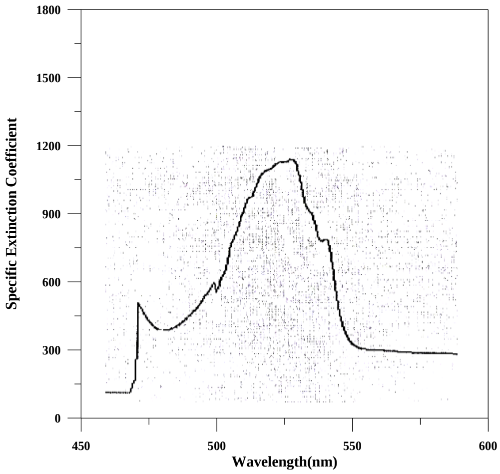


Figure (٢-١٩): Visible spectrum of anthocyanins [٩٠].

٢-٦-٤ Energy States of Chlorophyll:

Because of the large number of electronic configurations (which reflects the extensive double bonding through out the large molecule), chlorophyll absorbs light over a wide visible wavelength as well as the portion of the electromagnetic spectrum see Table (٢-١١). Absorption of an energetic photon takes chlorophyll from the "*ground*" state to a highly "*excited*" state. This highly excited state corresponds to the same lower excited state caused by the absorption of a red photon by a ground – state chlorophyll. This lower excited state is the one of interest. The energy represented by the lower excited state may be lose as fluorescence (which, overall, is a process of low magnitude, especially at low light, say, ٥٪ of lower excited state chlorophyll molecules return to ground state by fluorescence). As the preceding discussion caused you to infer, most of the chlorophyll molecules act as antenna to harvest light – they, themselves, are not involved in the light – driven oxidation – reductions that characterize photo synthesis. The bottom panel in this overhead shows that an in coming photon excites an antenna chlorophyll molecule. The excitation energy is transferred by a "*random walk*" to another chlorophyll molecule, and so forth, until the excitation energy is transferred to the special reaction – center pigment, which, because of its location (and the energy represented by the excited state) can reduce an electron acceptor, in the process, of course, the chlorophyll becomes oxidized[١٢١].

Carotenoids have two roles in photosynthesis. They, themselves, harvest light in the roughly ٤٣٠-٥٣٠nm range. Their excitation energy can be passed along to chlorophyll a (to push it to lower excitation state). Because they absorb further into the green than do chlorophylls, the contributions to photosynthesis can be significant. A second role of carotenoids is in their protective role against damage caused by light in the presence of oxygen (precisely those conditions that obtain in plants). A third electronic – state rearrangement of chlorophyll is possible. This third state, derived from the "lower excited state" that was discussed, can be deactivated by energy transfer to carotenoids, which can lose the energy nondestructively.

In the absence of carotenoids, the third state of chlorophyll reacts with $O_{٢}$, to form a highly reactive species (excited singlet oxygen) that wreaks havoc on unsaturated fatty acids (e.g. of membranes) and a host of other biomolecules. Any formed of the highly reactive species of $O_{٢}$ is "detoxified" (by conversion to ordinary $O_{٢}$) by carotenoids of the two protective roles of carotenoids, the quantitatively most important during photosynthesis is the deactivation of the third state of chlorophyll, and the lesser role is destruction of singlet oxygen [١٢٢,١٢٣].

٢-٧ Spectroscopic Methods:

Spectroscopy is the study of the interaction between electromagnetic radiation and matter; it is a phenomenon of quantum mechanic. Detailed information about structure and bonding, as wall as; about various intra-and intermolecular processes can be obtained from the analysis of atomic and molecular spectra [١٢٤].

٢-٧-١ Light:

Light is a form of electromagnetic radiation and, as such, exhibits properties of both a particle and a wave. The smallest quantized energy unit of electromagnetic radiation is called a photon.

White light can, therefore, be considered to consist of waves in motion. These wave posses a variety of wavelengths, each corresponding to a different color. The waves vibrate in all directions but are always perpendicular to the direction of the source.

Phenomenologically, the absorption of light can be described by Beer-Lambert's law. The intensity of the incident radiation ($I.$) will be only partly transmitted (I) through the material; the logarithm of the transmittance ($T=I/I.$), is proportional to the thickness of the layer (ℓ) and to the concentration of the absorbing component (c)

$$A= - \mathrm{Log}\ T = \mathrm{Log}\ I./I = \epsilon \ell c \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (٢-٥)$$

Where the proportionality factor is the absorption coefficient (ϵ) [١١٧,١٢٤].

٢-٧-٢ Electromagnetic Radiation:

Electromagnetic radiation, of which light is a sub classification, is usually described by either its frequency υ which is the number of waves per second, or its wave length λ which is the distance between waves, generally given in centimeters (*cm*). The product of frequency and wavelength is the speed of light *c* which is a constant: $c = \lambda\upsilon$. Electromagnetic radiation is composed of individual units (which are wave particles) of energy, called quanta; their energy is related by the equation: $E = hc/\lambda$, where *h* is Planck's constant.

The spectrum of electromagnetic radiation is shown is in Table (٢-١١). The visible region represents just a small fraction of the spectrum. In the visible region, the lower end corresponds to violet light at ٤٠٠nm, and the long end at ٨٠٠nm corresponds to red light; the various colors associated with visible light are shown in Table (٢-١٢)[٧٩].

Table (٢-١١): Regions of Electromagnetic Radiation Spectrum [٧٩].

Region	***Wavelength*** λ
Cosmic rays	٥×١٠^{-٥}nm
Gamma (γ) rays	$١٠^{-٣}$-٠.١٤nm
X- rays	٠.٠١-١٥nm
Far ultraviolet	١٥-٢٠٠nm
Near ultraviolet	٢٠٠-٤٠٠nm
Visible	٤٠٠-٨٠٠nm
Near infrared	٠.٨-٢.٥μ
Vibrational infrared	٢.٥-٢٥μ
Far infrared	٠.٠٢٥-٠.٥mm
Microwave radar	٠.٥-٣٠٠mm
Various radio frequencies	٠.٣-١m

Table (٢-١٢): Relationship between absorption and color in visible region [٧٩].

Wavelength Absorbed (nm)	*Color of Light Absorbed*	*Apparent Visible Color*
٤٠٠	Violet	Yellow
٤٥٠	Blue	Orange
٥٠٠	Blue-green	Red
٥٣٠	Yellow-green	Violet
٥٥٠	Yellow	Blue
٦٠٠	Orange-red	Green-blue
٧٠٠	Red	Green

Molecules are constantly undergoing molecular motions that are classified as vibrational motions or rotational motions. With UV light there is sufficient energy to cause transitions between the electronic energy levels in molecules, thus providing the basis of UV spectroscopy. In the IR region there is enough energy to measure the stretching and bending of bonds, thus resulting in IR spectroscopy [٨٠].

٢-٧-٣ **UV Spectroscopy**:

UV spectroscopy is an instrumental method for measuring electronic transitions within molecules. As Table (٢-١١) the UV and visible regions of the electromagnetic spectrum are adjacent to one another. Depending on the molecule being studied, absorptions may occur in either or both the UV and visible regions. Usually UV spectroscopy involves absorption of energy that is not visible to the naked eye.

The principles of a UV spectrophotometer are similar to those of an IR spectrophotometer, where the sample under study is dissolved in a suitable organic solvent and placed in a cell, while pure solvent is placed in another cell. Typical solvents for UV spectra are methanol, ethanol, acetone…etc., which is transparent to UV radiation. The light source is usually a hydrogen lamp, and the optics and cells are made of quartz because most other clear materials absorb UV energy. The light passes through both cells, and the net amount of energy absorbed is recorded on a chart paper in the manner described momentarily.

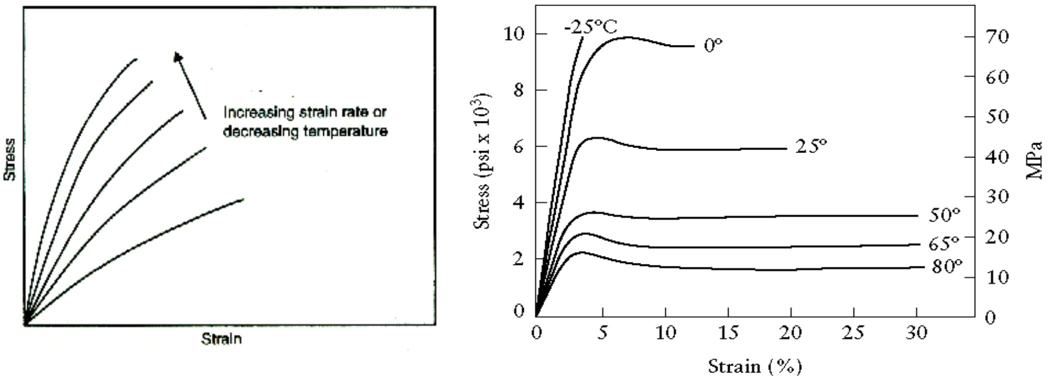
Several factors govern the amount of incident light or energy absorbed by a sample. One of these is the structure of the compound being studied. Another is the number of molecules in the sample, which depends on the concentration of the compound and the length of the cell that is used. The relationship among absorbance, concentration and cell length may be expressed by the Beer – Lambert Law [٧٩,١٢٥].

٢-٨ Mechanical Properties:

The important considerations to limit the usages of polymer materials are the mechanical behaviors including the deformation of the material by the applied stress which may be stationary as in case of creep test or mobile as in case of impact test. Each type of the polymer materials is characterized by definite properties which differ from that of other. This is due to presence of two kinds of bonds, the chemical bonds between the chain atoms and the van der waal bond between the polymer chains. The mechanical properties to define the good parts which are manufactured from these materials [١٢٦].

٢-٨-١ Viscoelasticity:

Polymer properties exhibit time – dependent behavior, which is dependent on the test conditions and polymer type. Fig (٢-٢٠) a and b are the typical viscoelastic response of a polymer to changes in testing rate or temperature. Increases in testing rate or decreases in temperature cause the material to appear more rigid, while an increase in temperature or decrease in rate will cause the material to appear softer.



(a) (b)

Figure (٢-٢٠): (a) Effect of strain rate on Mechanical behavior [١]. (b)Effect of temperature on the stress-strain curve for a thermoplastic polymer [١٩].

This time – dependent behavior can also result in long – term effects such as stress relaxation or creep. These two times – dependent behaviors are shown in Fig. (٢-٢١). Under a fixed displacement, the stress on the material will decrease over time, and this is called stress relaxation. This behavior can be modeled using a spring and dashpot in series as depicted in Fig. (٢-٢٢). The equation for the time dependent stress using this model is:

$$\sigma(t) = \sigma_0 e^{\frac{-t}{\tau}}$$

.... (٢-٦)

Where τ is the characteristic relaxation time (η/E). Under a fixed load, the specimen will continue to elongate with time, a phenomenon termed creep, which can be modeled using a spring and dashpot in parallel as seen in Fig. (٢-٢١). This model predicts the time – dependent strain as [١,١٢٧].

$$\varepsilon(t)=\varepsilon_0 e^{\frac{-t}{\tau}} \quad \text{..} \ (٢\text{-}٧)$$

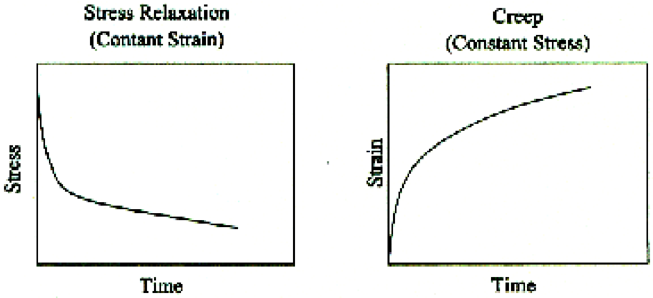


Figure (٢-٢١): Creep and stress relaxation behavior [١].

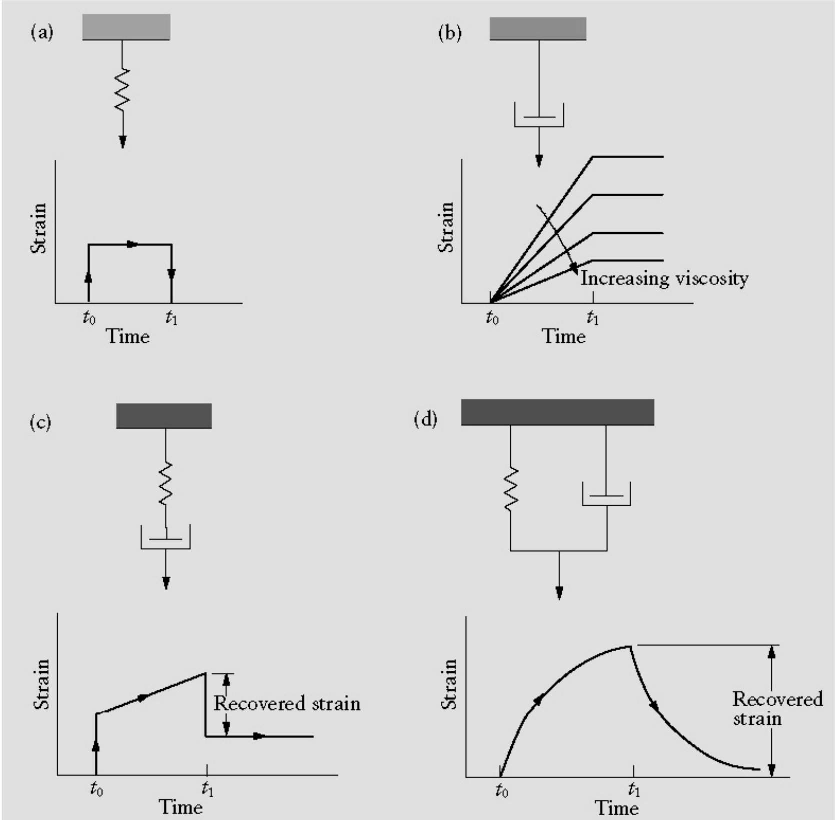


Figure (٢-٢٢): Various deformation modes for polymers (a) elastic,(b) viscous,(c) viscoelastic (Maxwell model),(d) viscoelastic (Voigt or Kelvin model)[١٠٧].

٢-٨-٢ Tensile Test:

Tensile Test can be used with a plastic test pieced to obtain stress-strain data Fig. (٢-٢٣).

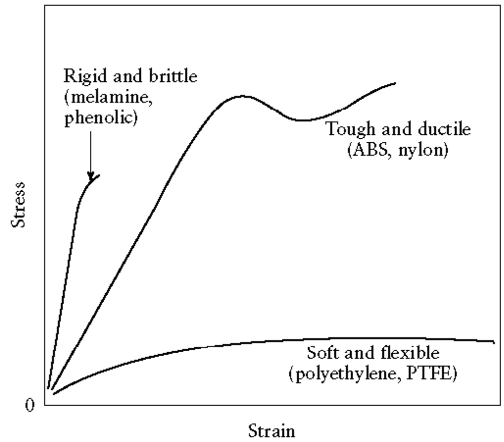


Figure (٢-٢٣): General term inology describing the behavior of three types of polymers [١٩].

Some information on material strength can be obtained from simple tensile stress-strain behavior. Material that fail at rather low elongations (١٪ strain or less) can be considered to have undergone brittle failure. Polymers that produce these types of failure include general purpose polystyrene and acrylics. Failure typically starts at a defect where stresses are concentrated. Once a crack is formed, it will grow as a result of stress concentration at the crack tip. Many amorphous polymers will also exhibit what are called crazes. Crazes look like cracks, but they are load bearing, with fibrils of materials bridging the two surfaces as shown in Fig. (٢-٢٤). Crazing is a form of yielding that, when present, can enhance the toughness of a material.

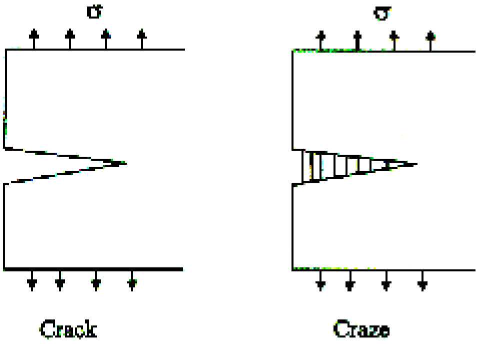


Figure (٢-٢٤): Cracks and crazes [١].

Ductile failure of polymers is exhibited by yielding of the polymer or slip of the molecular chains past one another. This is most often indicated by a maximum in the tensile stress – strain test or what is termed the yield point. Above this point, the material may exhibit lateral contraction upon further extension, termed necking. Molecules in the necked region become oriented and result in increased local stiffness. Material in regions adjacent to the neck are thus, preferentially deformed and the neck region propagates. This process is known as cold drawing see Fig. (٢-٢٥). Cold drawing results in elongations of several hundred percent [١,١٢٧].

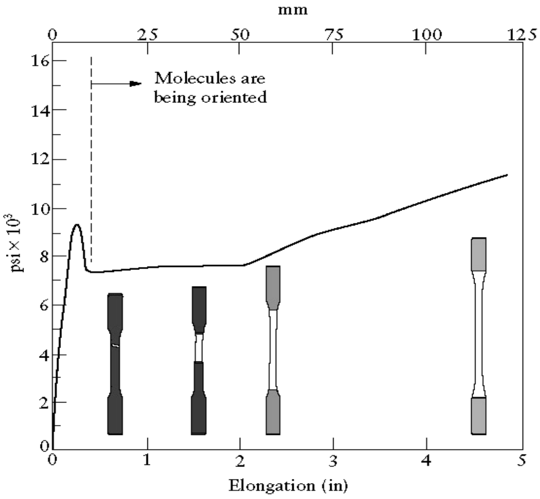


Figure (٢-٢٥): Load –elongation curve for thermoplastic [٦٩].

٢-٨-٣ Fracture Mechanism:

Fracture is the appearance of new two surfaces in a body as a result of its effect by external force and is divided into two parts, research Brittle and Ductile fracture.

In the first type no any deformation occurs before fracture and the beginning of fracture occurs out of deformation region, thus the cross section before and after fracture is nearly equal as in case of the glass. Brittle Fracture depends on temperature of the sample stress is applied to, and its properties.

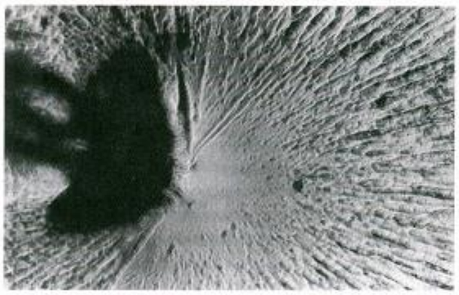
While the second type is formed after clear deformation in the body or in some of its sites before separation into two parts. Separation starts from the inside of the medium in which deformations dispersed and the parts after fracture are not similar in the cross area as before fracture [١٢٨,١٢٩].

Fig (٢-٢٦) a scanning electron micrograph shows an example of **a** brittle fracture surface in a cross-linked polyester and Fig. (٢-٢٦ **b)** shows schematically the different regions that compose such a surface. There are three regions:

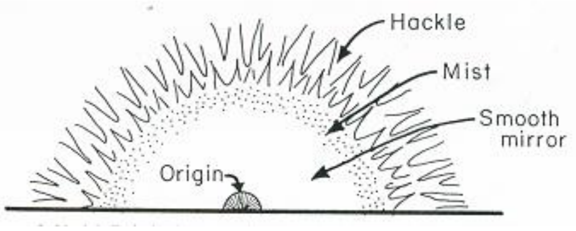
a – A mirror like or specular region adjoining the crack nucleation site, indicating slow crack growth.

b – A coarse and flat region indicative of fast crack growth, some times called hackle, and one can see that the crack has propagated on different levels over small areas. When hackle is elongated in the direction of crack propagation, the pattern is called "river markings".

c – A transitional region between the preceding two that has a misty appearance and no resolvable features [٧١].



a



b

Figure (٢-٢٦): a- Brittle fracture in a highly cross-linked thermoset

b- The three different regions that compose the brittle surface in a [٧١].

٢-٨-٤ Impact Tests:

Impact tests are designed to simulate the response of a material to a high rate of loading and involve a test piece being struck a sudden blow. There are two main forms of test the Izod and charpy tests. Both involve a pendulum Fig. (٢-٢٧) swinging down from a specified height h_o to hit the test piece and fracture it. The height h to which the pendulum rises after striking and breaking the test piece is a measure of the energy used in the breaking, and it is possible to calculate from the following relation:

Impact strength=Energy required for Crack/Sample cross sectional area...(٢-٨)

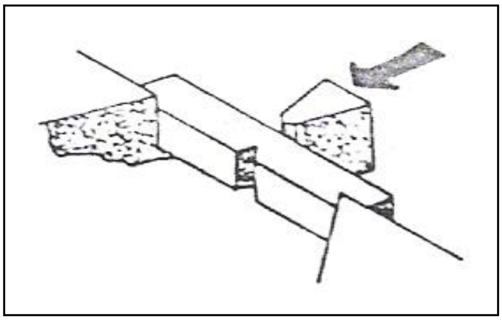


Figure (٢-٢٧): Charpy impact testing technique [٧١].

Impact strength depends on various variables including type of the materials, temperature, stress system, strain rate, manufacture, and geometry of article, fabrication and environment conditions [١,١٠٩].

٢-٨-٥ Bend Tests:

The materials are in the forms of beams and bent by three – point bending Fig. (٢-٢٨). The term flexural strength or modulus of rupture is used for the surface stress in the beam when breaking occurs. For a beam, the stress σ at distance *Y* from the neutral axis is related to the bending moment M and the second moment of area *I* of the beam section by $\sigma/y = M/I$. with three-point loading M=FL/٤. For a rectangular cross-section beam I=bd٣/١٢, where *b* is the breadth of the section and *d* its depth. The maximum stress will occur at the surface when y=d/٢. Thus, for a rectangular cross-section beam [١٣٠].

$$FlexuralStregth = \frac{3FL}{2bd^2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2-9)$$

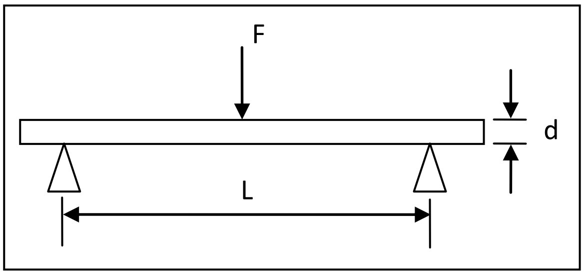


Figure (٢-٢٨): A bend test that can be used to determine the flexural strength [١٠٩].

٢-٨-٦ Hardness Tests:

The hardness of a material may be specified in terms of some standard test involving indenting or scratching of the surface of the material, the harder a material the more difficult it is to make on indentation or scratch. There is no absolute scale for hardness, each hardness form of test having its own scale.

The Brinell, Vickers and Rockwell tests can be used with plastics. Rockell test widely used scale R and ball of diameter ٢.٣٨mm.

In other form of test that is used is the shor durometer. This is a hard – held device which involves a rounded indenter [١٠٩].

٢-٩ Thermal Properties:

Thermal properties that are generally of interest in the selection of materials include how much a material will expand for a particular change in temperature and how – good a conductor of heat it is.

$$\text{*Linear expansivity } \alpha\,(K^{-١}) = \frac{\text{Change in length}}{\text{Original length} \times \text{change in}} \quad (٢\text{-}١٠)$$

Is a measure of the amount by which a length of material expands when the temperature increases.

$$\text{* Heat Capacity } C\,(\text{J kg}^{-١}\ K^{-١}) = \frac{\text{Amount of heat}}{\text{Mass} \times \text{change in temperature}} \quad (٢\text{-}١١)$$

The amount of heat needed to raise the temperature of a block of material by ١*K*.

$$\text{*Thermal Conductivity } k\,(\text{Wm}^{-١}K^{-١}) = \frac{\text{Quantity of heat / second}}{\text{Temperature gradient}} \quad (٢\text{-}١٢)$$

Is a measure of the ability of a material to conduct heat [١٠٩].

The thermal conductivity is defined in terms of the quantity of heat that will flow per second divided by the temperature gradient which measured according the flowing formulae.

$$q=-kA\left(\frac{\Delta T}{\Delta X}\right)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{٢}-1)$$

q = quantity of heat /second

k = thermal conductivity

A = cross section area

ΔT/ΔX = temperature gradient

Chapter Three

Experimental Part

٣-١ Materials Used:

Three different types of polymers are used in this work, thermoset and thermoplastic polymers which are mentioned below. The polymers which were choosing commercially are very important and widely used in applications now. All these polymers are exposed to many factors during their used, such as, chemicals and atmosphere (sunlight, humidity, heat … etc).

٣-١-١ Epoxy Resin(ER):

The epoxy (thermoset resin) that is used by LEYCO – POX ١٠٣ type which has low viscosity. Two – component epoxy resin system with formulated polyamine hardener. Technical data for this resin is listed in Table (٣-١).

Table (٣-١): Technical data for epoxy resin [١٣١].

Mixing ratio : By weight	A : B = ٧ : ٣
Density at ٢٣°C g/cm^{٣}	١.٠٥
Linear shrinkage %	٠.٣
Volume shrinkage %	٣.٥

Note: A = epoxy resin B = hardener

٣-١-٢ Unsaturated Polyester (UPE):

This thermoset polymer available locally without detail specifications. The mixing ratio used was ١٠٠g of UPE resin with ٠.٥g accelerator (Cobalt napthenate) and ٢g hardener (Methyl Ethyl Ketone peroxide).The main properties listed in Table (٣-٢).

Table (٣-٢): Technical data for UPE [١٣١].

Mixing ratio : By weight	A : B = ١٠٠ : ٢
Density at ٢٣°C g/cm^{٣}	١.١٥
Linear shrinkage %	٠.٨

Note: A = UPE B = hardener

٣-١-٣ Poly (Vinyl Chloride) (PVC):

Two kinds from PVC were used in this research; the first PVC is a thermoplastic polymer available locally in the National chemical and plastic industries Co.S.A.Baghdad. It is granulating type Sc/٨٥ and its specification is given in Table (٣-٣). The second UPVC was available locally and the properties are given in Table (٣-٣).

Table (٣-٣): PVC specification [١٣٢].

Properties	*PVC*	*UPVC*
Hardness	Showr ٦٥ ±.٣٥	Brinell ٠.١٥
Specific Weight	١.٣٥	١.٣٨
Tensile Strength MPa	١٥	٥٢
Elongation %	٤٤٠	٢٨

٣-٢ Natural Pigment Extraction:

Natural pigment is extracted from fresh plant leaves, flowers, and roots by solvent. The solvent was chosed according to pigment polarity. The chlorophyll and β- carotene were extracted by acetone, while anthocyanin pigment it is water – soluble, due to its high polarity. Extraction of pigments was carried on in the laboratory according to be suitable process introduce by us. The result shows that, it is suitable be a commercial extraction process.

٣-٢-١ Chlorophyll:

Chlorophyll extracted from Celery by acetone according to the following procedure:

١- Cleaning the Celery leaves and dried at temperature ٤٠°C.

٢- Milling the dry Celery leaves then mixing with acetone (each ١g Celery powder in ٥ ml acetone).

٣- Filtering the solution by cotton cloth, the extracted pigment solution stored in the refrigerator waiting to treat with polymer later.

٣-٢-٢ β- carotene:

The fresh yellow flowers are chopped in a mortar then mix with excess acetone in amount that covered all the flowers and the agitation continue for half hour and the mixture left about ٢٤ hours. The solution filtrating to remove the unsoluble part by using cotton fabric, and stored in the refrigerator to use.

٣-٢-٣ Anthocyanins:

The Chards gives a better result than other plants [٥٦], so, the anthocyanins content extracted from it by water. First cutting the chard root into thin slices and mixing them with water for ٢٤ hour, then filtering the solution by cotton cloth and stored it in order to be used. All pigments extracted are shown in Fig (٣-١).

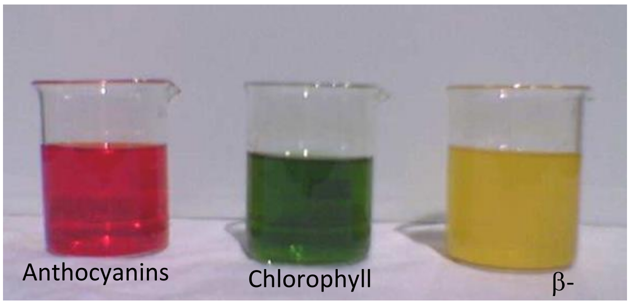


Figure (٣-١): Extracted pigment.

٣-٢-٤ Determination of Pigment Concentration:

Drying ١ml from the pigment solution by evaporation the solvent then weigh the remainder. The pigments concentration is listed in Table (٣-٤).

Table (٣-٤): Pigments Concentration.

Pigment	***Concentration g/ml***
Chlorophyll	٠.٠١٣٨
β- Carotene	٠.٠٢٧٢
Anthocyanins	٠.٠٩٦٦

٣-٣ Samples Preparation:

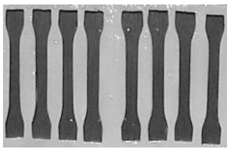
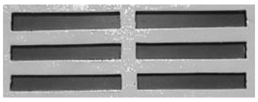
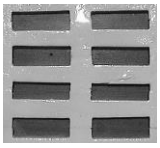
In this work two types of polymers are used, thermoset resin and thermoplastic polymers. They are different in samples preparation and their testing due to their differences as precursor material and properties. The thermost type obtained as resin paste but the thermoplastic as granules.

٣-٣-١ ER and UPE:

٣-٣-١-١ Mould preparation:

For preparing samples for all tests for this work, one mould for each test required. Each mould consists of three parts, the middle part with a dimension listed in Table (٣-٥) which contains equivolume spaces (this design give us the ability to moulded eight sample with different concentration with same specification) while the other two parts one of them act as a base and the other its cover to adjust the mould dimension. Mould release materials are used (wax and polyvinyl acetate).All dimension listed in Table (٣-٦).

Table (٣-٥): Moulds for testing.

Test type	***Mould***
Tensile	
Bending	
Impact	
Hardness and Thermal Conductivity	

٣-٣-١-٢Mixture preparation (Polymer and Pigment):

a- The required quantity of pigment solution is dried (by evaporating the solvent).

b- Add the pigment to the resin and mixed with addition of the proper quantity of accelerator and hardener until a homogeneous viscous material obtained.

c- After complete mixing, the viscous material casts in the mould and leaving for ٢٤ hr. until solidification.

d- Heating at ١٠٠°C for ١ hour to insure complete curing.

٣-٣-٢ PVC:

١- Immersion the PVC granules with pigment solution in the required percent. The PVC will be absorbed all the solution then PVC granules were swelled.

٢- Exposure the PVC granules to the atmosphere to evaporate solvent and the PVC granules return back to its nearly original volume. The result is the pigment diffused into PVC particles. Fig. (٣-٢) shown PVC particles are colored by different pigments.

Anthocyanins

Chlorophyll

β-

Figure (٣-٢): Colored PVC particles.

٣- (a)-Plasticized poly(vinyl chloride):

Converting the PVC particles to pasts by using laboratory mill type schwabeuthan polymix ١٥٠P at ٨٠°C, as shown in Fig. (٣-٣). Take the materials from the mill as a sheet. To homogenize the sheet thickness, is used hydraulic press type HYD.P. ١٥٠٠٠ kp Fig (٣-٤). The sample pressed under pressure ٤٢ kp /cm^{٢} at ٨٥°C for ٢٠ min. The sheet pressed with mould consists of three parts, the middle part dimension of ٢٠٠×٢٠٠×٥ mm shown in Fig (٣-٥).

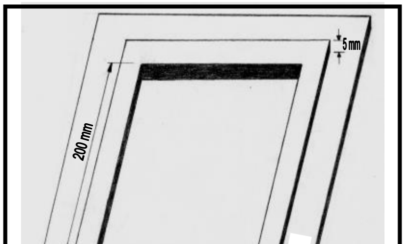


Figure (٣-٣): Laboratory mill. Figure (٣-٤): Hydraulic press. Figure (٣-٥): Mould of test samples.

Two test samples were cut from the sheet. The cutting was made by using hand press type Wallace Test Equipment as shown in Fig. (٣-٦).

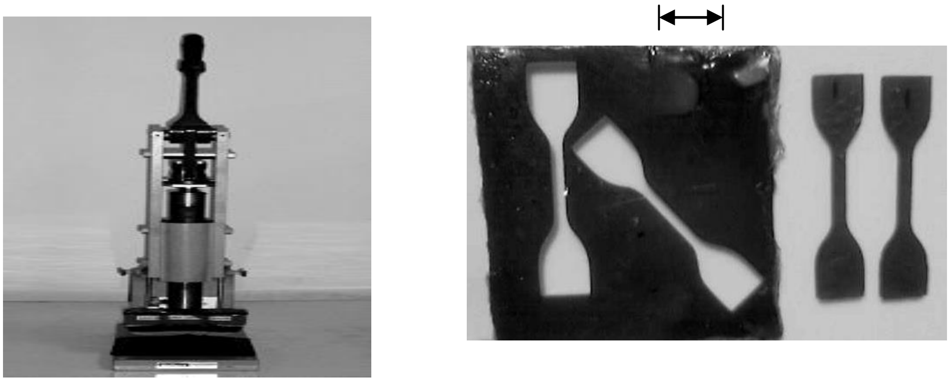


Figure (٣-٦): a) hand press. b) Sheet after cutting and specimen.

(b)- UnPlasticized poly (vinyl chloride):

١٠ g from UPVC pressed using hand press type (Simpliment II) with pressure ٢.٥MPa and temperature ١١٠°C Fig (٣-٧). The sample pressed for ٢ hours for complete homogeneity.

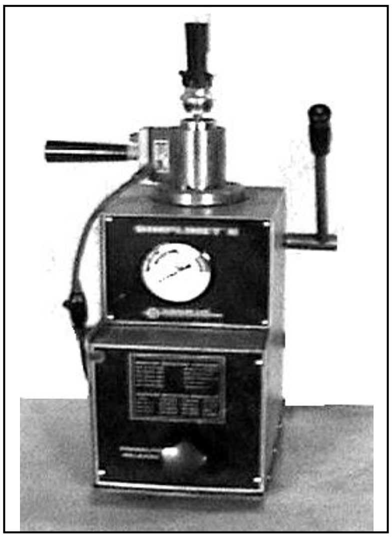


Figure (٣-٧): Hand press.

٣-٤ Environmental stability:

In this work pigments are also used as stabilizers and colorants for polymers. In environmental test such as, exposure to heat, UV, humidity and atmosphere are carried for both blank samples and samples after addition of pigments. A comparison takes place between the two results due to the lack of literature for such comparison.

٣-٤-١ Exposure to heat:

Samples for tensile, flexural, and hardness are heated at ١٢٥°C in oven type PHOENIX ١٥D Dry rod. Weight loss, color change, surface examination and mechanical properties are determined as a function of time.

٣-٤-٢ Exposure to UV:

Samples for hardness test are exposed to UV-radiation from UV source works on ١٦ watt (٣٨٠ kJ mol $^{-١}$) and wave length ٣٧٥-٣٨٠ nm, which is shown in Fig (٣-٨). Weight loss, surface examination, color change and hardness are determined as a function of a time.

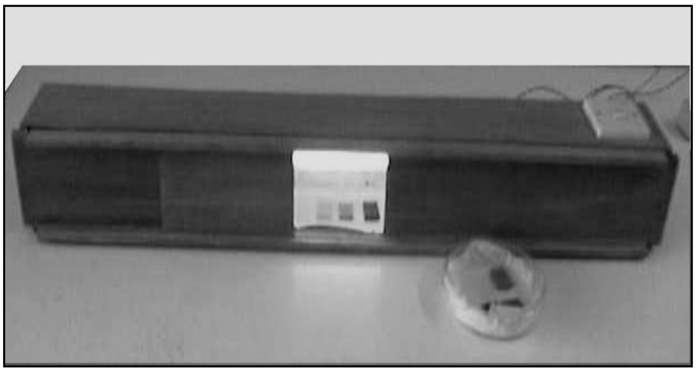


Figure (٣-٨): UV-Lamp.

٣-٤-٣ Exposure to Atmosphere:

Samples for flexural and hardness test are exposed to atmospheric weather as a function of time to determined the effect on mechanical properties upon exposure to the atmosphere.

٣-٥ UV – Spectroscopy Test :

UV- Visible spectrometer is used, type Cintra ٥ GBC Scientific Equipment, it's shown in Fig (٣-٩). The sample dimensions are ٦٠×١٤×١.٥mm. The aim of this test is to identify the absorption band and their shift due to the mixing of the pigments and the polymers.

Figure (٣-٩): Citra ٥ UV-Visible spectrometer.

٣-٦ Mechanical Tests:

Tensile, flexural, impact and hardness tests are carried out to determine the mechanical properties of the samples. All tests were performed at room temperature.

٣-٦-١ Tensile Tests:

The sample is positioned vertically with the aid of the grips of the testing machine, which were tightened evenly and firmly by using sand paper to prevent any slipping during the tension procedure.

٣-٦-١-١ ER and UPE samples:

Tests are carried out on samples which are prepared as shown in Table (٣-٦). Instron universal testing machine (Model ١١٩٥) Fig (٣-١٠) is used. The rate speed is (١ mm/min) with max. load ٥ kN.

٣-٦-١-٢ PVC sample:

Monsanto T١٠ tensometer machine is shown in Fig (٣-١١) it used special jaws for holding tensile test sample which is movable at speed ٥٠٠ mm/min with the stress range ٥٠ Mp_a and the strain range ١٠٠٠٪. The sample dimension is given in Table (٣-٦).

Figure (٣-١٠): Instron universal testing machine.

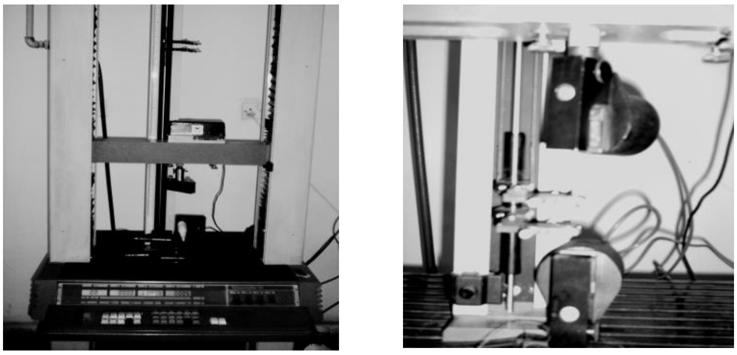


Figure (٣-١١): a) Monsanto T١٠ Tensometer. b) jaw for tensile.

٣-٦-٢ Flexural Test:

The load technique for flexural test is shown in Fig (٣-١٢). PHYWE universal testing machine is used, with the test speed (٠.٠٥ mm/min). The supports span ٩٠ mm (the distance between the supports), was depending on the sample thickness. Table (٣-٦) illustrates the sample dimensions.

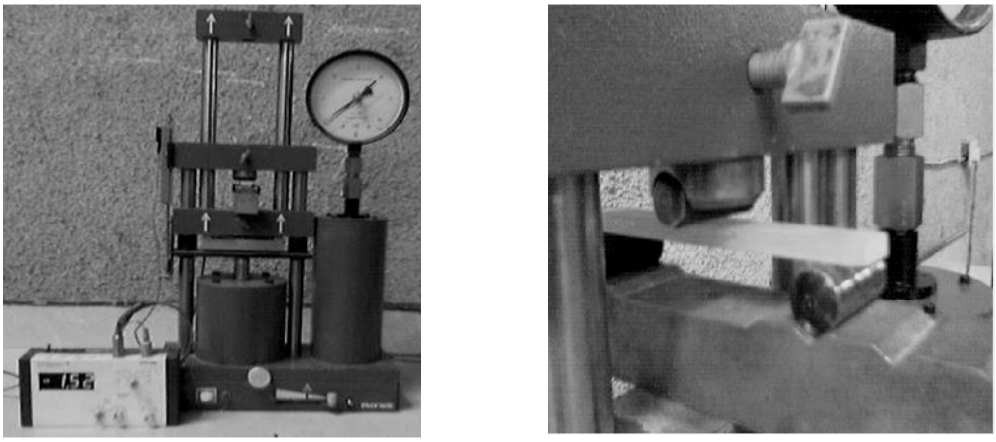
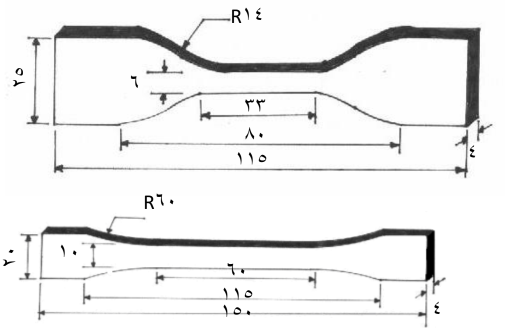
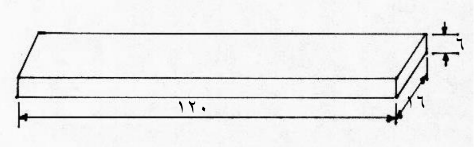
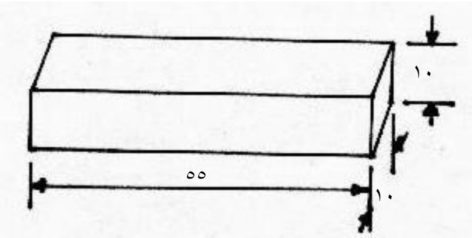
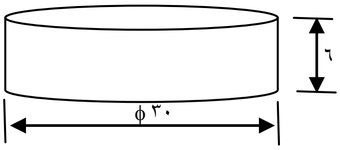


Figure (٣-١٢): The loading Technique for flexural test.

Table (٣-٦): Illustrates samples test dimension.

	Tensile	***Material***	***Sample***	***ASTM***

١	Tensile	PPVC ER + UPE		D ٤١٢ – ٨٨ D ٦٣٨ – ٨٧
٢	Flexural	ER + UPE		D ٧٩٠ – ٨٦
٣	Impact	ER + UPE		D ٢٥٦ – ٨٧
٤	Hardness – Shore – Briell	PVC,		D ١٤١٥ D ٧٨٥

Note: All dimensions in mm.

٣-٦-٣ Impact Test:

Charpy impact testing machine is shown in Fig (٣-١٣) is used. The sample is impacted by a pendulum hammer (٥ Joules). Table (٣-٦) shown unnotched sample dimension.

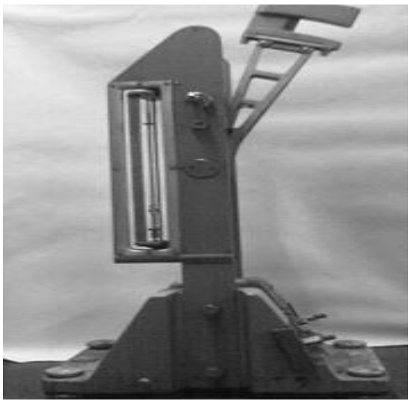


Figure (٣-١٣): Charpy impact testing machine.

٣-٦-٤ Hardness Test:

Hardness measurements an empirical, comparative test of the resistance of the material to plastic deformation.

- ER, UPE, and UPVC:

Brinell hardness is used for these thermoset polymers. The tester type PHYWE universal testing machine shown in Fig (٣-١٤) is used.

- PVC:

Shore hardness test is used in measurement of the penetration of rigid ball into the PVC thermoplastic samples under specified condition. ١٠٠ shore A type zwick shown in Fig (٣-١٥) is used. The scale of measurement so chosen that zero represents a material having elastic modulus equal to zero and ١٠٠ represents a material of infinite elastic modulus, thus the scale covers all the normal range of hardness.

٣-٧ Color Shade:

Mikrospec-eval-٣٠ program is used to find color shade according to the ASTM-D ٤٠٣٩; it is taking ٠ degree to black and ٢٥٥ to white color.

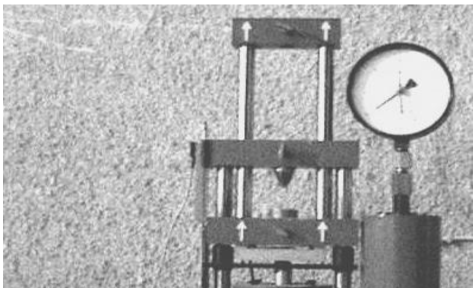


Figure (٣-١٤): The loading Technique for hardness test.

Figure (٣-١٥): Shore hardness tester.

٣-٨ Thermal conductivity:

Thermal conductivity measured by Lee's disk with the tester type P.A. Hilton S.N. H٩٤٠/os١٩٥. It's shown in Fig (٣-١٦).

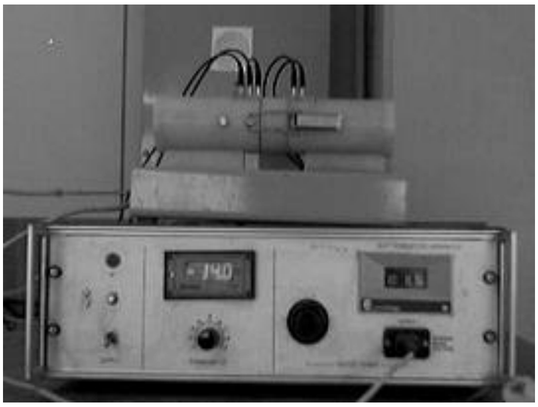


Figure (٣-١٦): Heat – conduction unit.

Chapter Four
Results and Discussion

٤-١ Introduction:

This chapter deals with all results and discusses them according to the changes of physical and mechanical properties caused by the effect of pigments (Chlorophyll, Anthocyanin, β- carottene) on the following polymers:

a. Epoxy resin(ER), unsaturated polyester (UPE) and poly (Vinyl chloride) (PVC) with chlorophyll pigment.
b. Epoxy resin and unsaturated polyester with anthocyanin.
c. Epoxy resin and unsaturated polyester with β – carotene.

٤-٢ Interaction and Reaction:

The addition of natural pigments to the polymers is a fresh subject with poor literature. Thus, a comparison was used to study the physical and mechanical properties of the polymers between samples with and without pigments.

The extracted pigment (Chlorophyll, Anthocyanin, and β – carottene) are added individually to the ER and compared that with pure ER. The additions of Chlorophyll and Anthocyanin shows the heat emission (exothermic reaction) and the mixture solidify with irregular shape increasing i.e. vigorous reaction took place while the ER with its hardeners solidified in a uniform shape and without heat emission (see fig ٤-١). We conclude that, the functional groups in both pigments (C=O, CHO, COO, and OH) in addition to the double bonds make chlorophyll and anthocyanin to act as catalysts for such reaction because both of pigments remained unchanged in this reaction and that are clear of their color. β-carotene shows no reaction and no heat emision during mixing this is due to the absence of functional groups in these molecules(see fig ٤-٢) [١٣٣,١٣٤].

٤-٣ Using the pigments as colorants:

Different ratios of chlorophyll to the polymers get different color shades, as shown in Fig (٤-٣) in spite of that, the used polymers are colorless. The ER and PVC plastic became as a green color, while the UPE become brown, which indicates that, there is a charge transfer complex formation result in color change from green to brown. While addition anthocyanin and β – carotene to the ER and UPE in different ratios also show color shade according to the ratio added as shown in Fig (٤-٤). Similar color shades were obtained by other workers [١٣٥, ١٣٦].

٤-٤ Environmental stability test:

The exposure of the polymers to heat, sunlight, humidity, aging during storage and technological processes results in color change, degradation and deformation of the polymer. Similar conditions provided by us on the ER, UPE, and PVC mixed with chlorophyll pigment to study the effect of this pigment on the stability of these polymers.

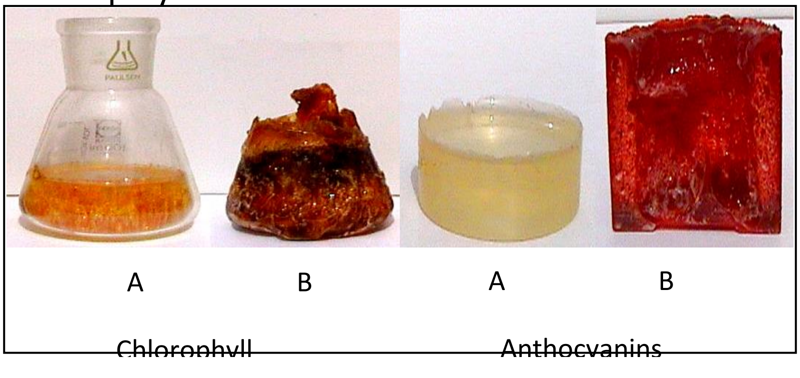
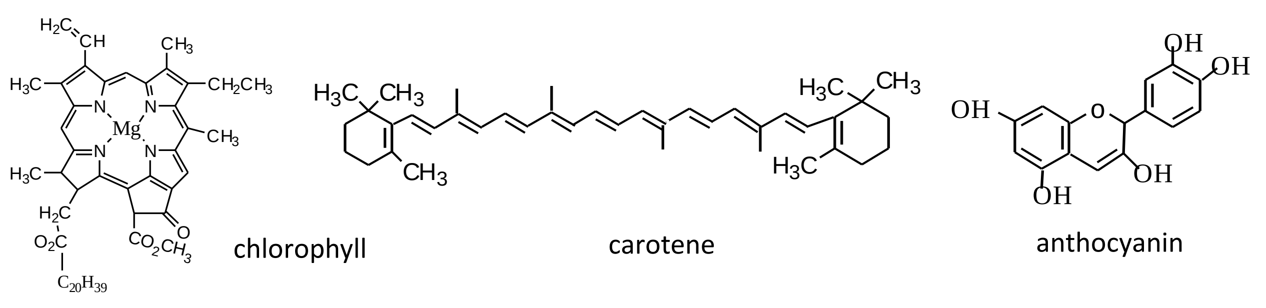


Fig (٤-١): Effect of Pigments addition on ER (A- blank sample B- with pigment).


chlorophyll

carotene

anthocyanin

Figure (٤-٢): shows pigments formulas [٧,١٢٠,١١٣].

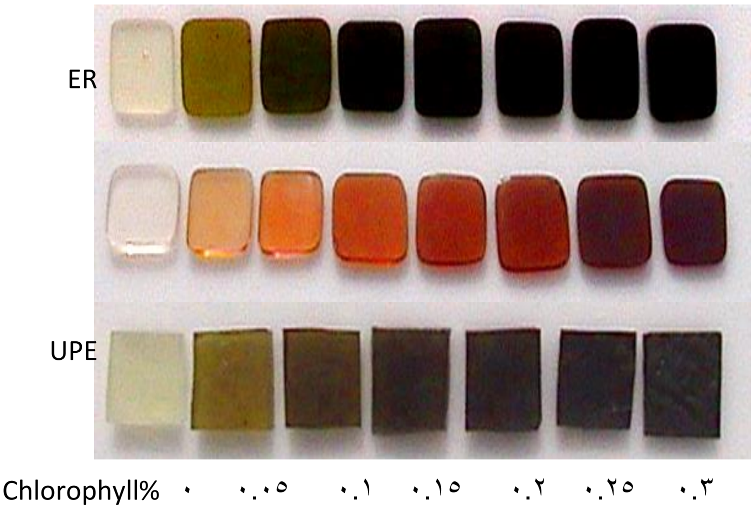


Fig (٤-٣): Addition of chlorophyll to the above polymers.

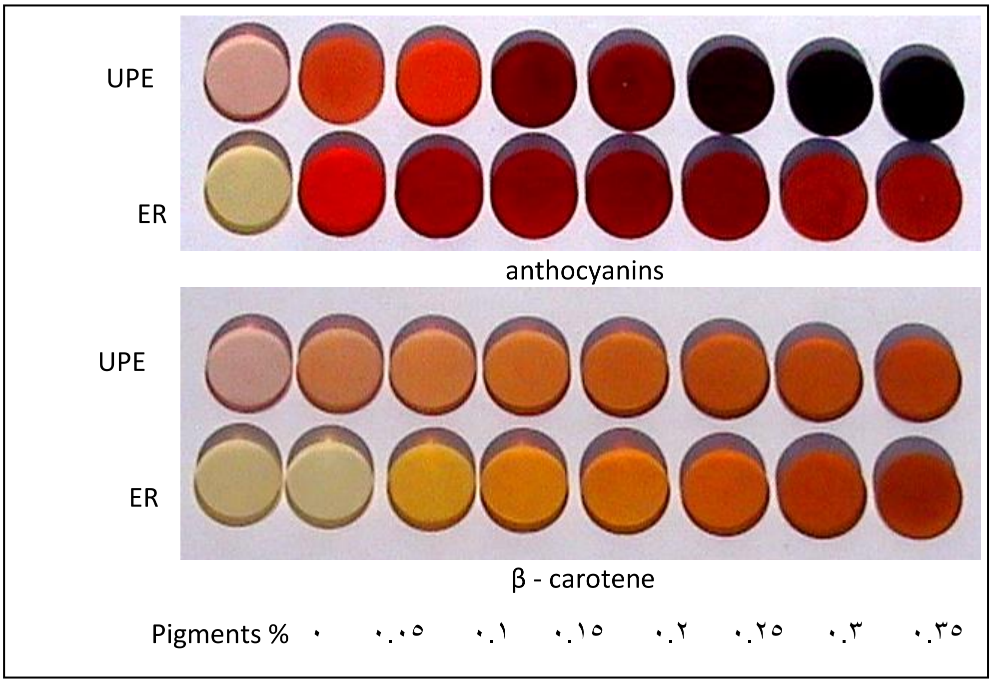


Fig (٤-٤): Addition anthocyanin and β – carotene to the polymer

٤-٤-١ Effect of Heat on Color Shade and Weight Loss:

The three polymers samples with and without chlorophyll are exposed to ١٢٠°C. This temperature is considered to be as a good accelerating test due to the large difference with the ambient temperature that polymer exposed to it.

Fig (٤-٥) shows the effect of temperature on polymers color, Figs (٤-٦) to (٤-٨) shows the effect of temperature on samples color shade. Without chlorophyll (pure samples) the color changes from colorless to brown. As the exposure time increases the color becomes deeper as well as cracking occurs in the polymer (see fig ٤-٩) this due to the oxidation of the pure polymer at the high temperature, while with the addition of chlorophyll no color change takes place, this is due to that chlorophyll act as heat absorber and anti oxidant material [١٣٧].

In case of PVC plastic the exposure to ١٣٠°C for long time (literature shows that the susceptibility to the thermal degradation of PVC reaches a critical level from a temperature above ٦٠°C [٣٧]). After ٧ days under the above temperature in air oxidation (blackening) starts from the edge of the sample and after ١٠ days completely blackening of the sample occur, while with chlorophyll oxidation starts after ١٢ days and completed after ١٧ days see Fig (٤-١٠). The heat stability improvement with chlorophyll is equal to ٧١.٤% when comparing with pure PVC.

Elongated time of polymers oxidation in the presence of the chlorophyll pigment is due to that chlorophyll protects polymers molecule from oxygen attack in the site in which chlorine atom liberated from the polymer molecule in two different ways:

a. Chlorophyll acts as antioxidant it link the site of departure chlorine atoms.
b. Chlorophyll acts as thermal absorber [١٣, ٩١].

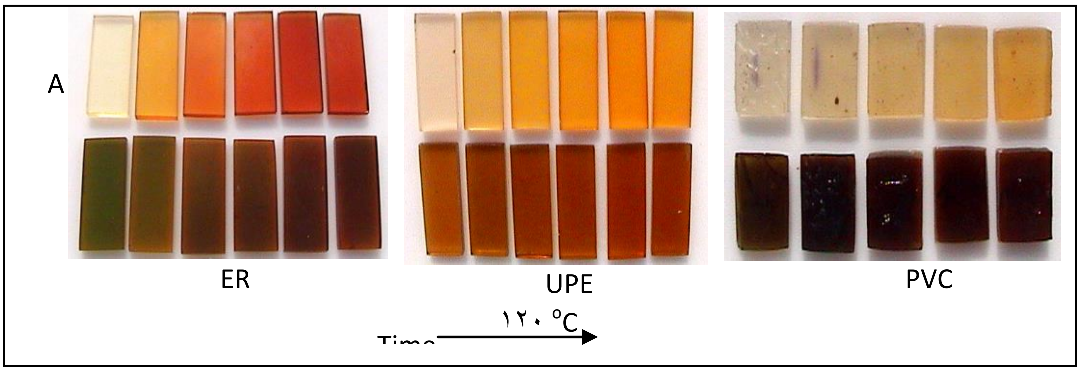


Fig (٤-٥): Effect of heat on polymers color (A- blank sample   B- with pigment).

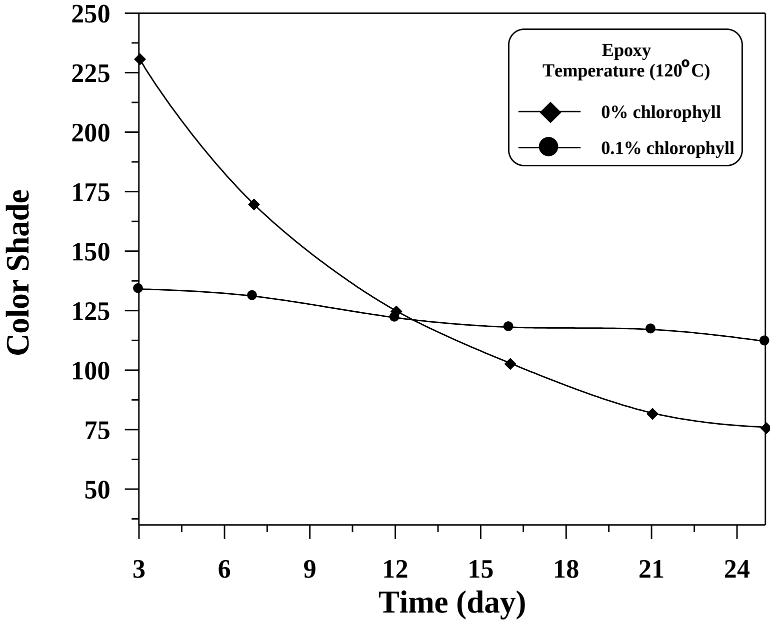


Fig (٤-٦): Effect of heat on polymers color shade.

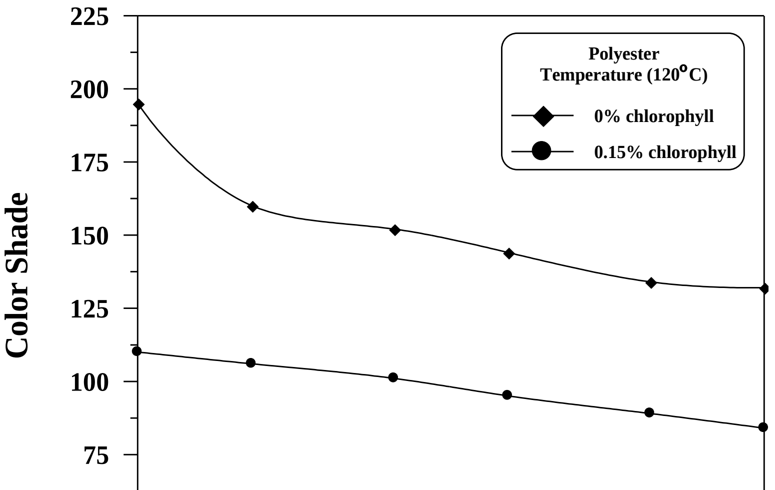


Fig (٤-٧): Effect of heat on polymers color shade.

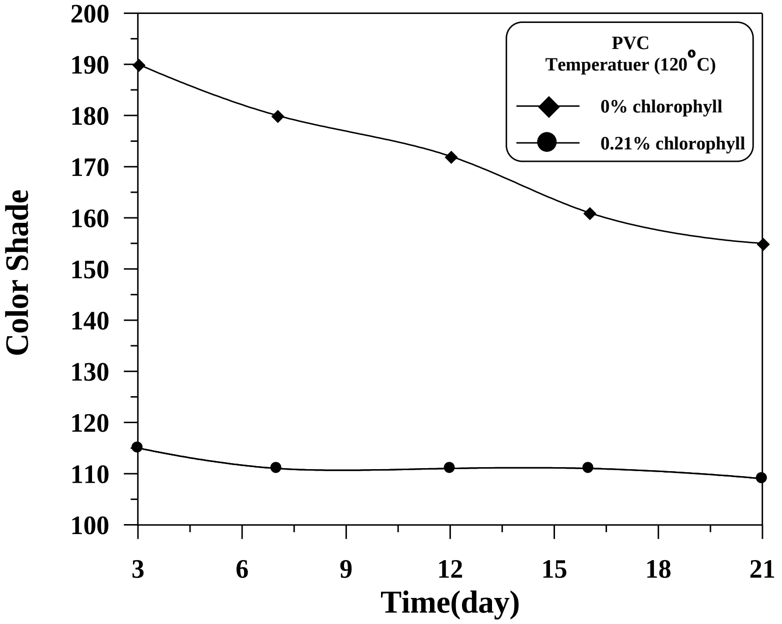


Fig (٤-٨): Effect of heat on polymers color shade.

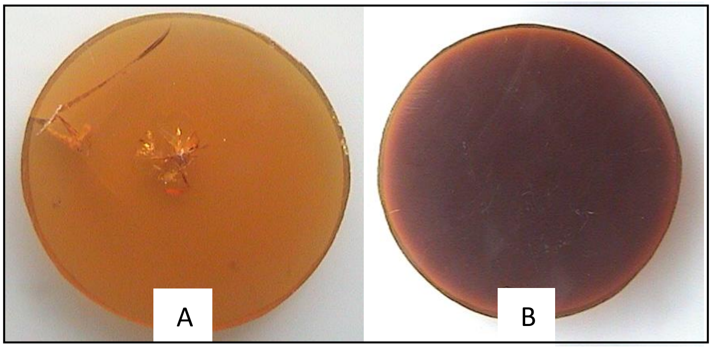


Fig (٤-٩): Cracking upon exposure to heat (A- blank sample B- with pigment).

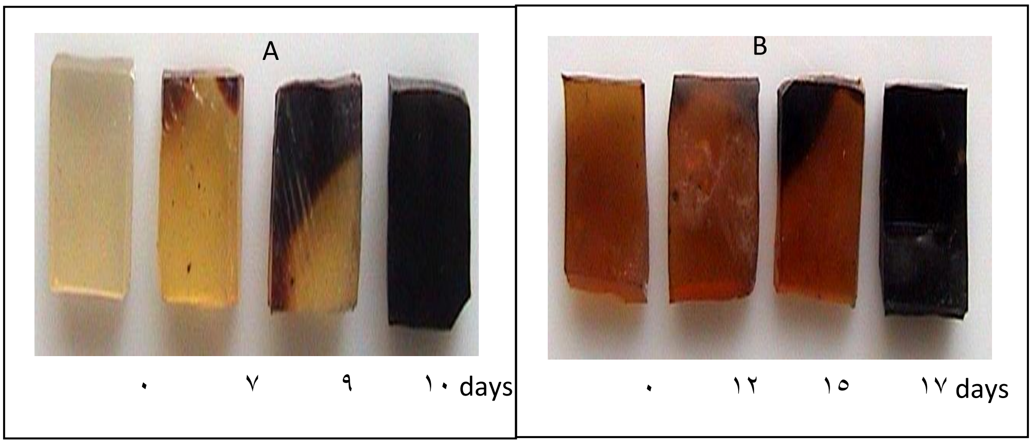


Fig (٤-١٠): Effect of heat at ١٣٠°C on PVC oxidation (A- blank sample B- withchlorophyll).

The effect of chlorophyll on the weight loss of polymers during exposure to ١٢٠°C was tested for ٢١ days. The addition of chlorophyll in small percent shows the depression in the weight loss of the polymers (the temperature and time choosed according to optimum experimental result obtained). The optimum quantity was ٠.١%, ٠.١٥%, and ٠.٢١٪ for the ER, UPE, and PVC respectively as defined from Fig (٤-١١) to (٤-١٣). Above these percent the weight loss increases which is explained as: In the low percent, chlorophyll acts as protector to polymer molecule as explained above while above this percent chlorophyll act as plasticizer (extended the distances between the polymer molecules, i.e. breaking the intermolecular forces between these molecules) which increases the probability of weight loss of the polymers upon heating due to lowering the T_g, T_m and increasing flowability of the polymer [١].

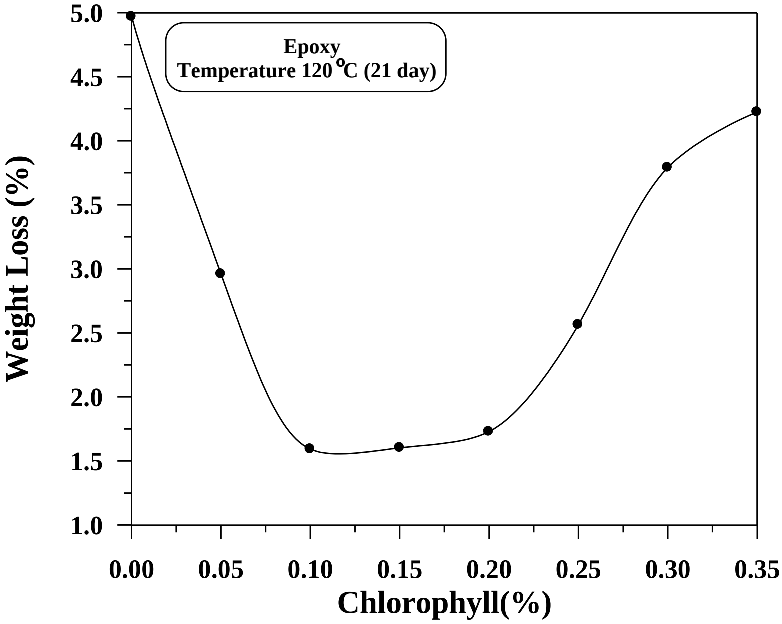


Fig (٤-١١): Relation between chlorophyll (%) and weight loss (%) at ١٢٠°C.

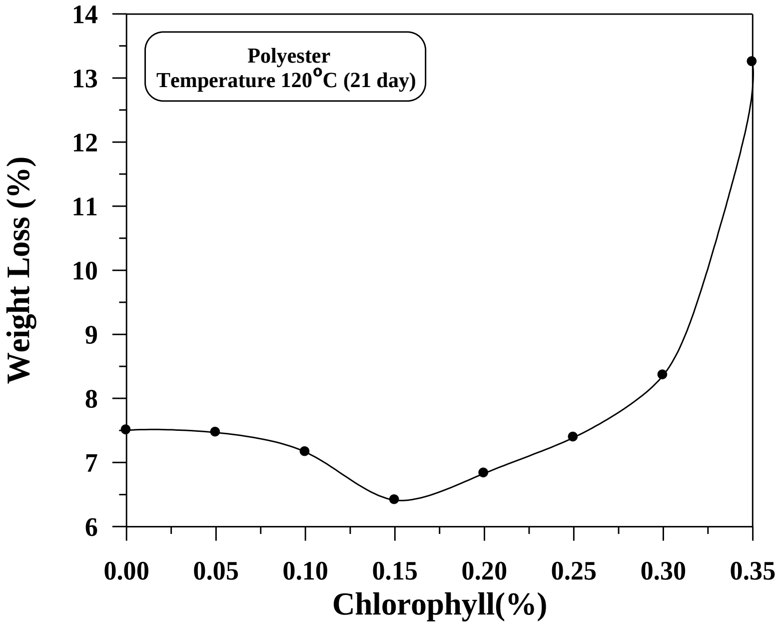


Fig (٤-١٢): Relation between chlorophyll (%) and weight loss (%) at ١٢٠°C.

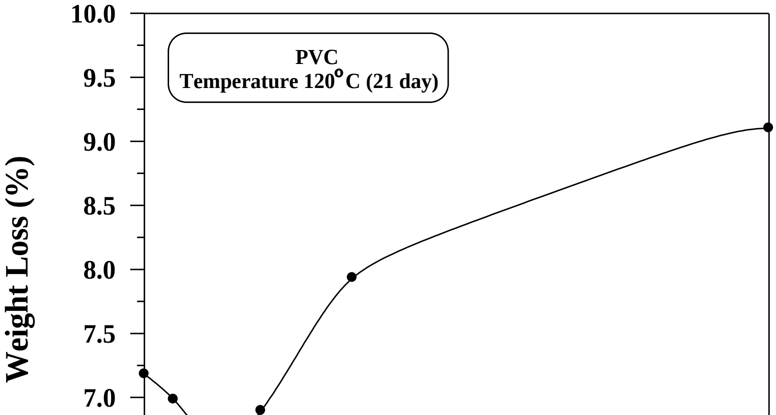


Fig (٤-١٣): Relation between chlorophyll (%) and weight loss (%) at ١٢٠°C.

Figs (٤-١٤) to (٤-١٦) show the effect of the chlorophyll optimum percent on the weight loss of the three polymers at different time. It seems clearly that the presence of chlorophyll with the polymer decrease its weight loss (the weight loss come from the polymer itself not from chlorophyll because results show that there was no weight loss from chlorophyll alone under this condition).

The efficiently of chlorophyll on the improvement of the stability of the studied polymers are shown in Table (٤-١).

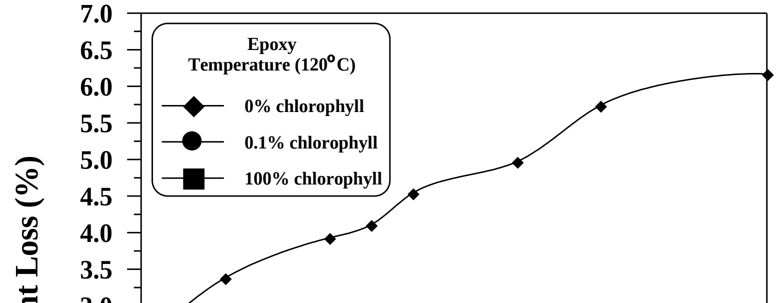


Fig (٤-١٤): Effect of time exposure on the weight loss (%) at ١٢٠ °C.

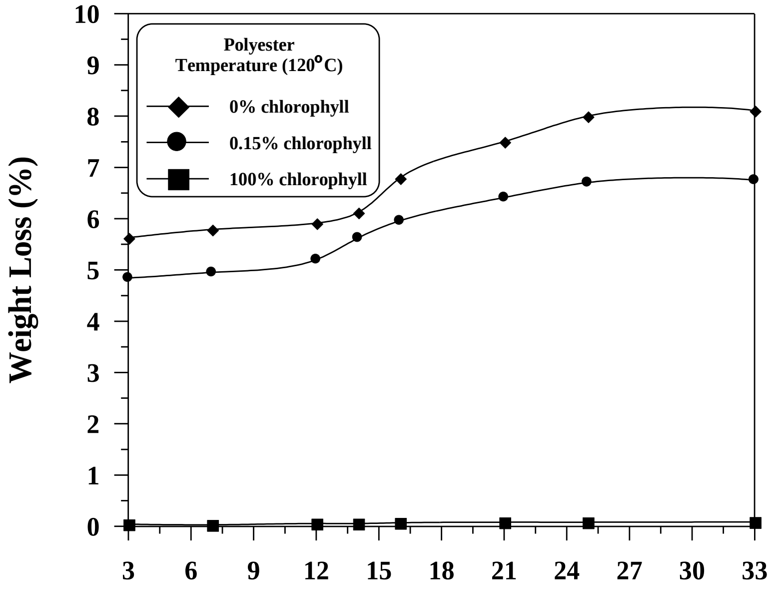


Fig (٤-١٥): Effect of time exposure on the weight loss (%) at ١٢٠ °C.

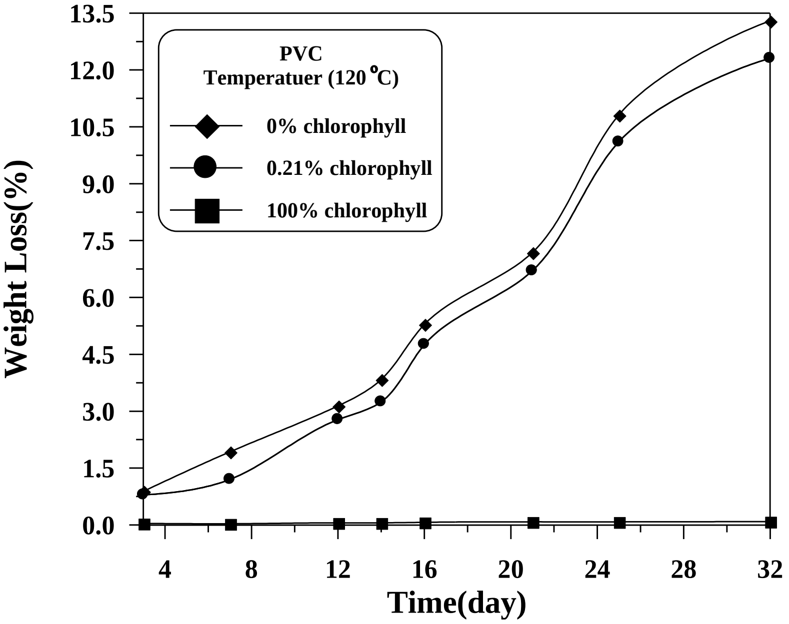


Fig (٤-١٦): Effect of time exposure on the weight loss (%) at ١٢٠ °C.

Table (٤ – ١): Percent improvement in weight loss of polymer samples.

polymer	*Chlorophyll (%)*	*Improvment percent in weight loss when exposed to*		
		Heat(١٢٠ °C)	*UV*	*Enviromental*
ER	٠.١	٢١٢.٢٥	٥١	٧٩.٦٧
UPE	٠.١٥	١٧	٣٥.٣٢	٧٣.٨٢
PVC	٠.٢١	٧.١٩	٤٣.٤١	٧٢.٢٢

٤-٤-٢ UV – Exposure on Color Shade and Weight Loss:

Samples of ER, UPE, and PVC are exposed to UV – light source in order to study the effect of this radiation on the polymer properties. Fig (٤-١٧) shows the effect of UV on the samples colors, Figs (٤-١٨) to (٤-٢٠) shows the effect of UV on the samples colors shade, with and without addition of chlorophyll.

Figs (٤-٢١) to (٤-٢٣) represent the weight loss under the effect of UV – light. The weight loss decreases with increasing the chlorophyll percent, a reflecting point a bear in which the weight loss starts to rises. This is due to that chlorophyll begins act as plasticizer. Figs (٤-٢٤) to (٤-٢٦) show chlorophyll as UV absorber result in lowering the weight loss in the polymer, comparing with pure polymer even with low percent of chlorophyll addition. Chlorophyll in this case absorbs UV light and changed it into harmless thermal energy [٣٧]. This mechanism similar in photosynthetic , the most of the chlorophyll molecules act as antenna to harvest light and convert this energy to heat used in photosynthetic process [١١٦,١١٧] . This means that chlorophyll has ability to protect polymers and worked as a stabilizer [١٣٥] .Table (٤-١) shows the stability improvement of studied polymers.

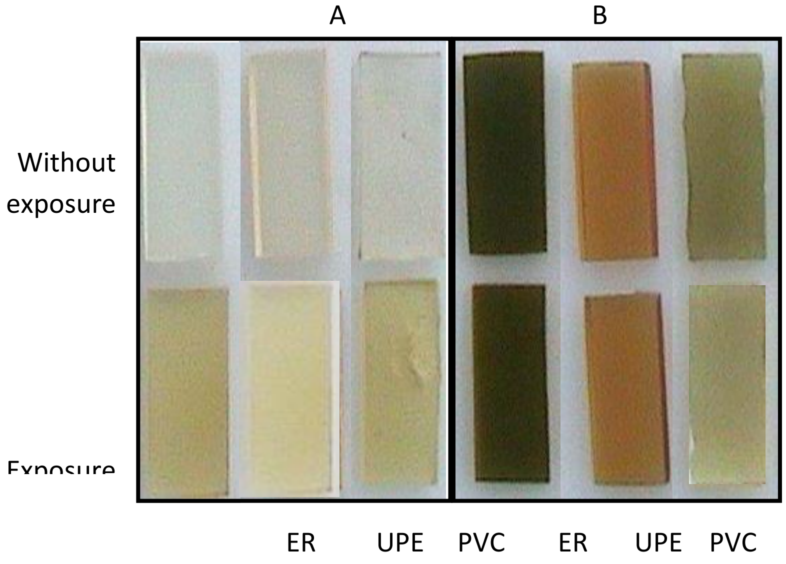


Fig (٤-١٧): Effect of UV-light for ٢١ day on polymers color (A- blank sample B- with chlorophyll).

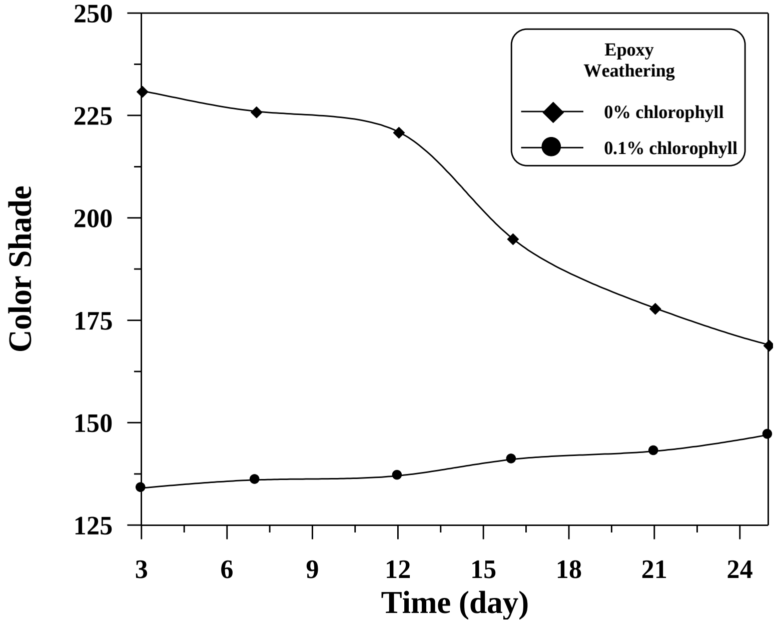


Fig (٤-١٨): Effect of UV-light on polymers color shade.

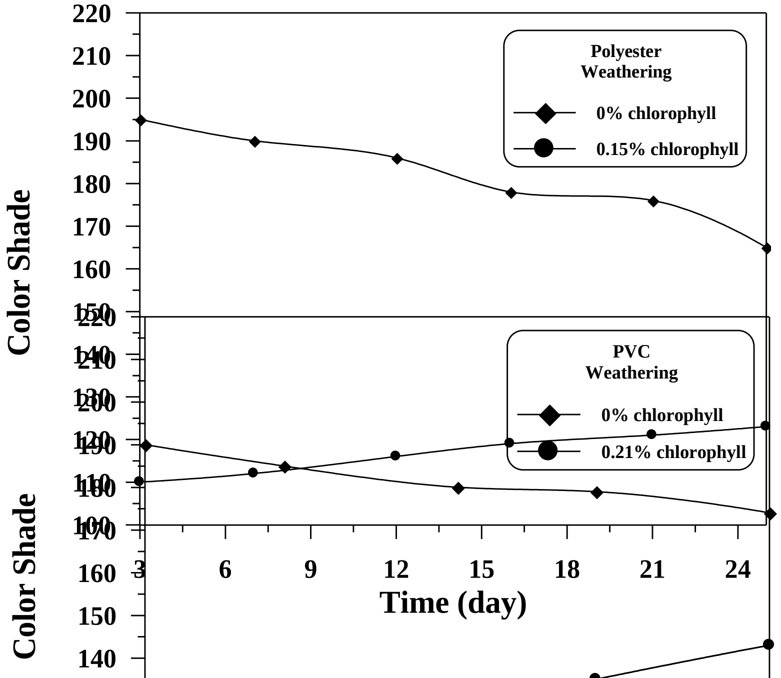


Fig (٤-١٩): Effect of UV-light on polymers color shade.

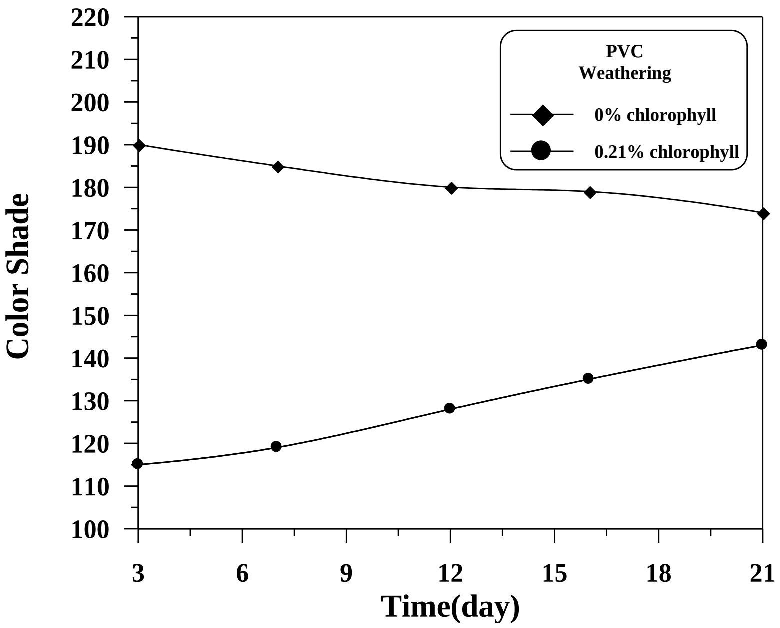


Fig (٤-٢٠): Effect of UV-light on polymers color shade.

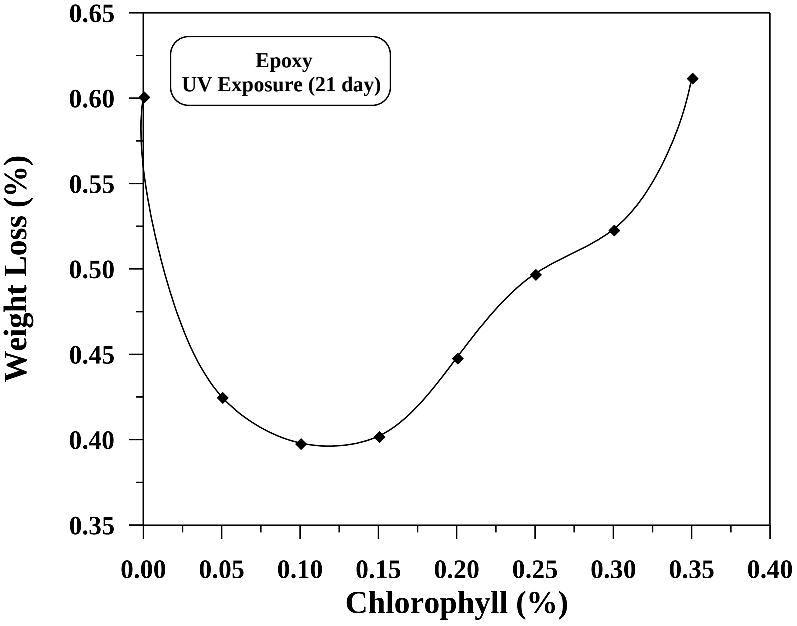


Fig (٤-٢١): Effect of chlorophyll (%) on weight loss (%).

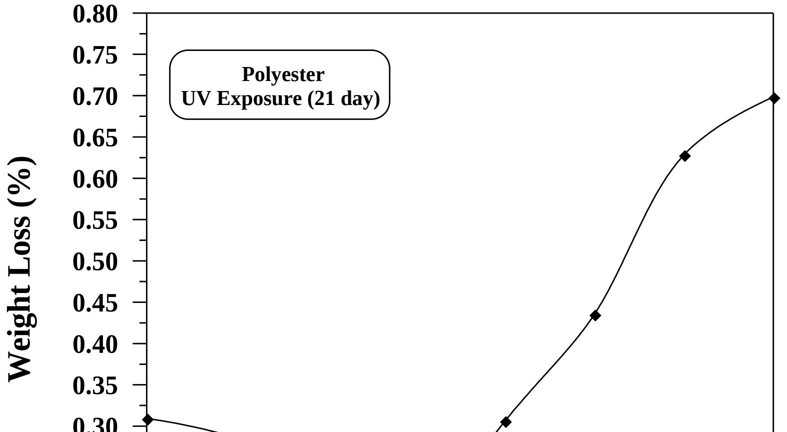


Fig (٤-٢٢): Effect of chlorophyll (%) on weight loss (%).

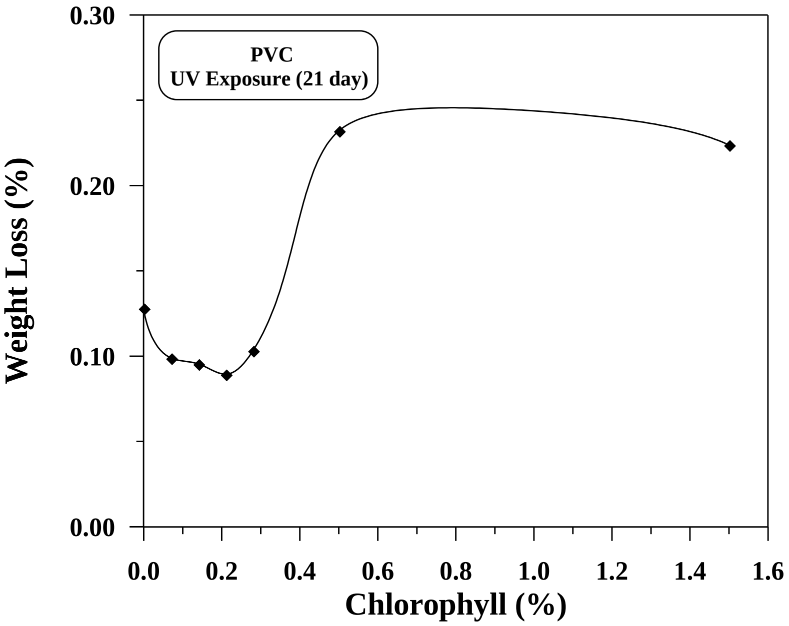


Fig (٤-٢٣): Effect of chlorophyll (%) on weight loss (%).

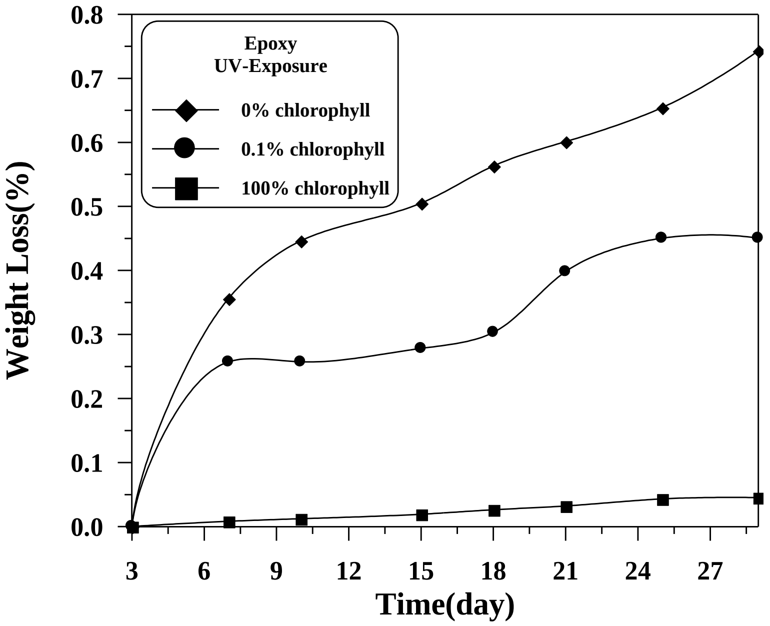


Fig (٤-٢٤): Effect of time exposure on weight loss (%).

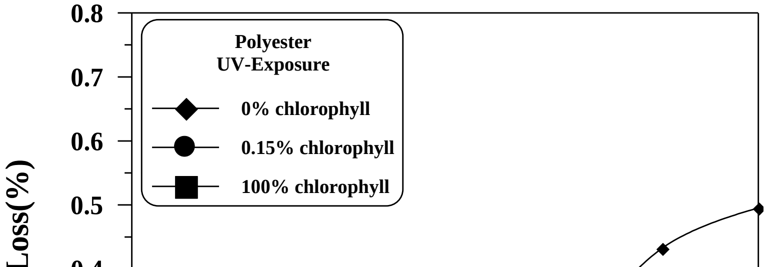


Fig (٤-٢٥): Effect of time exposure on weight loss (%).

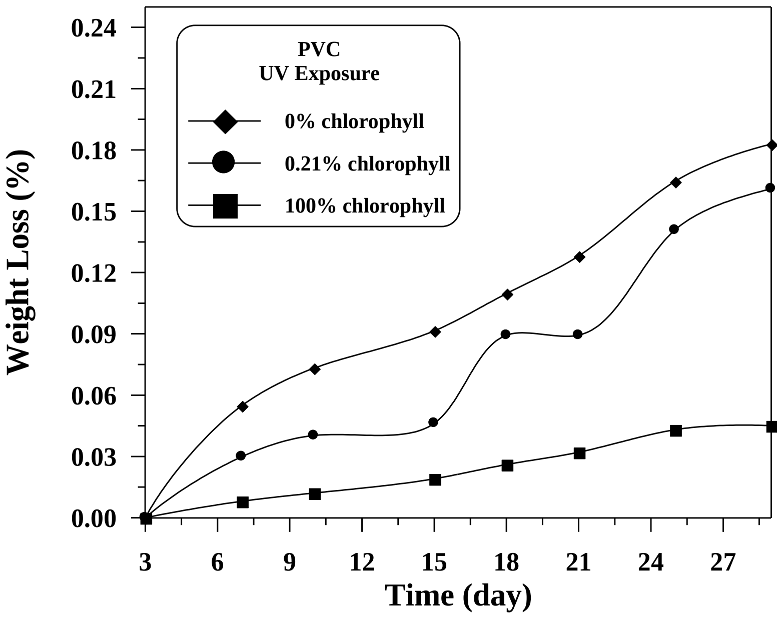


Fig (٤-٢٦): Effect of time exposure on weight loss (%).

٤-٤-٣ Environmental Exposure:

Fig (٤-٢٧) shows the effect of environmental on polymers color; Figs (٤-٢٨) to (٤-٣٠) shows the effect of environmental on polymers color shade. Without chlorophyll the sample color change from colorless to brown. As the exposure time increases the color becomes deeper, while with chlorophyll lower environmental effect on samples color occurs.

Figs (٤-٣١) to (٤-٣٢) show the effect of exposure time on the samples weight loss with the optimum chlorophyll percent. The result in this test is similar with the other two accelerated tests (heat and UV tests). We conclude from that, the chlorophyll acts as a good UV protection as well as a stabilizer (anticracker). The stability improvements of the studied polymers are shown in Table (٤-١).

Fig (٤-٢٧): Effect of atmosphere exposure on polymers color (A- blank sample B- with chlorophyll).

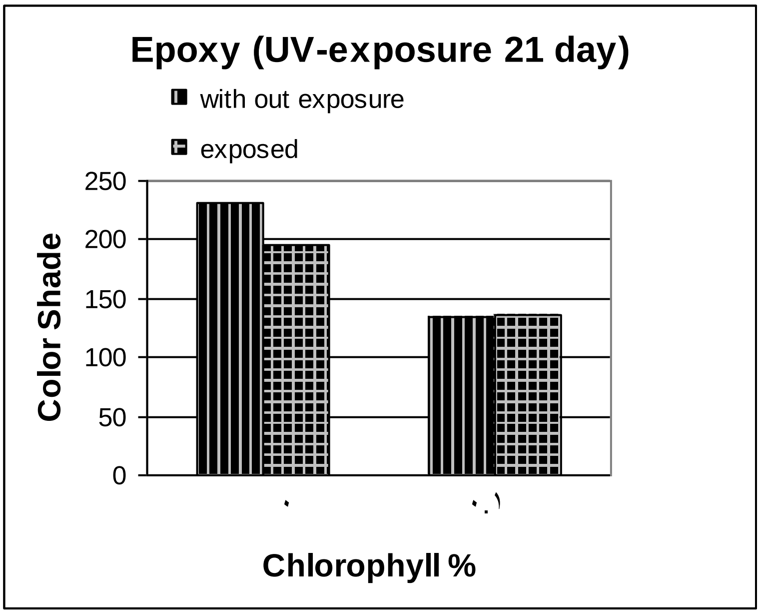


Fig (٤-٢٨): Effect of atmosphere exposure on polymers color shade.

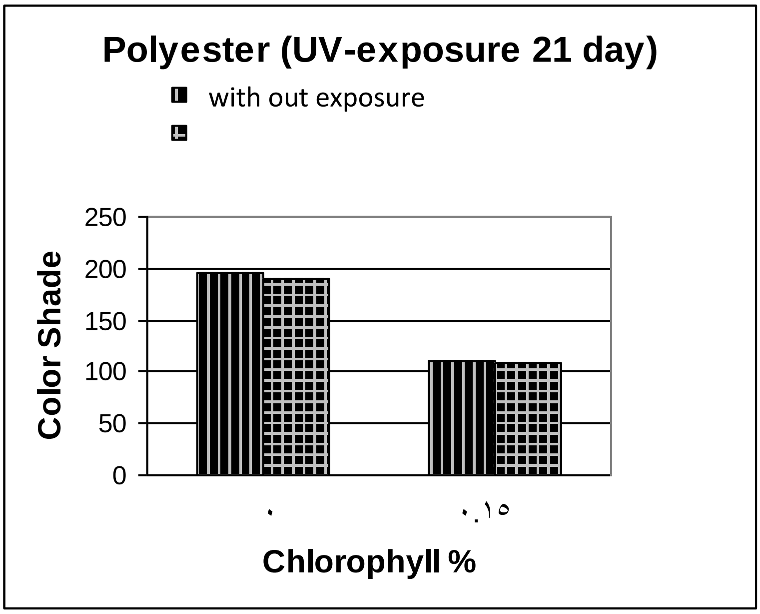


Fig (٤-٢٩): Effect of atmosphere exposure on polymers color shade.

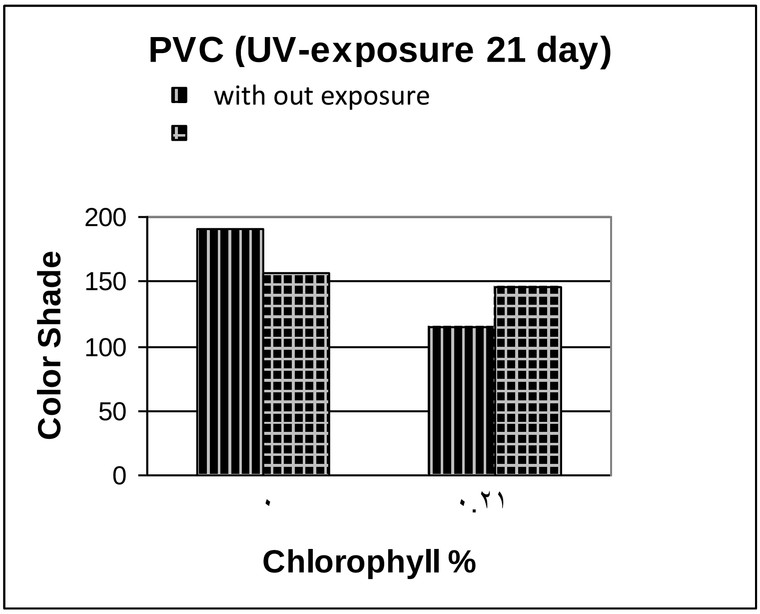


Fig (٤-٣٠): Effect of atmosphere exposure on polymers color shade.

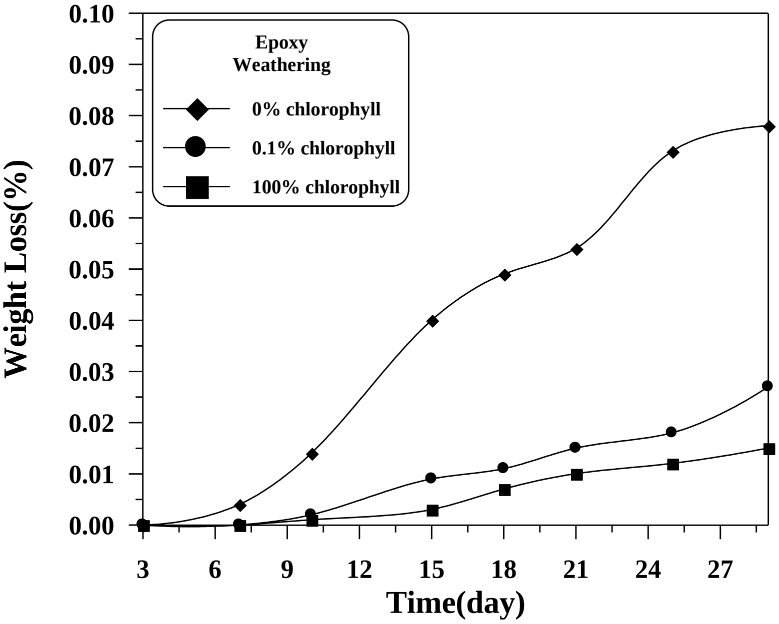


Fig (٤-٣١): Effect of atmosphere exposure on weight loss (%).

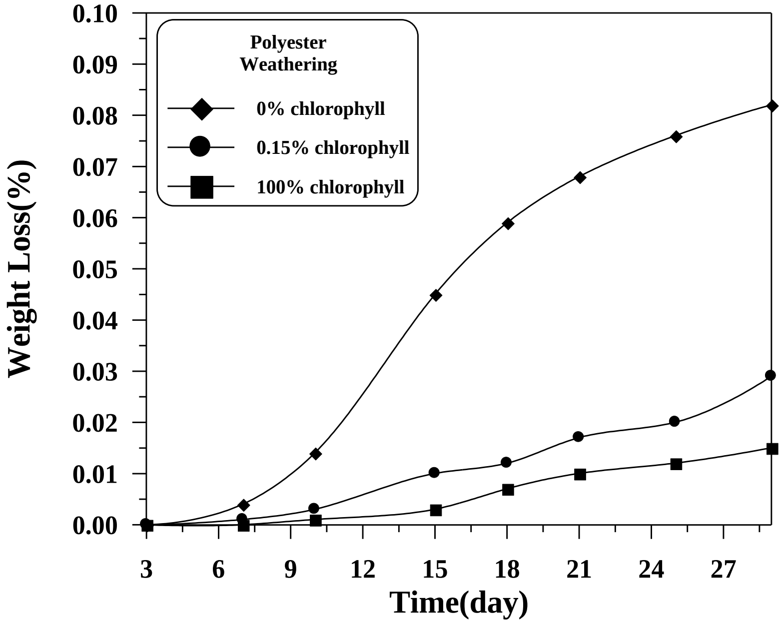


Fig (٤-٣٢): Effect of atmosphere exposure on weight loss (%).

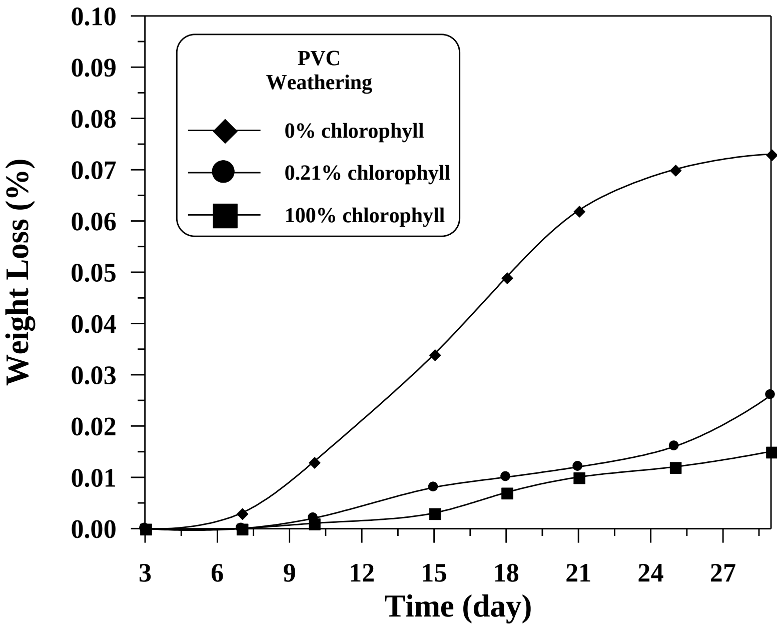


Fig (٤-٣٣): Effect of atmosphere exposure on weight loss (%).

٤-٥ UV –Visible Spectroscopy test:

Figs (٤-٣٤) to (٤-٣٩) show the absorption spectra of pure chlorophyll, pure polymer, and their mixtures in range ١٨٠-٨٠٠ nm.

Chlorophyll shows two absorption bands in the visible region (٤٦٥ and ٦٦٤ nm). The longer wavelength one is due to the $n \longrightarrow \pi^*$ transition of lone pair electrons on nitrogen atoms (Mg coordination system), and the second one is due to the extended conjugated diene system [١٣٨,١٣٩].At low concentration of chlorophyll with epoxy the first bond of chlorophyll slightly shift to the lower wavelength while in case of increasing the concentration this band sifted to the longer wavelength. This is due to increasing the interaction of the double bond in the chlorophyll with the epoxy. While the other bands ٦٦٤nm shifted also to longer wavelength due to the interaction of the lone pair electrons with epoxy. With the UPE the chlorophyll band (٤٦٥nm) highly shifting to the shorter wavelength (higher energy), this indicates charge transfer from the UPE to the chlorophyll to the π bond. While the second bond (٦٦٤nm) completely disappear due to highly interaction in the UPE. With PVC the two bands of the chlorophyll show slightly change with the PVC which indicates that week interaction with comparing with the other two polymers.

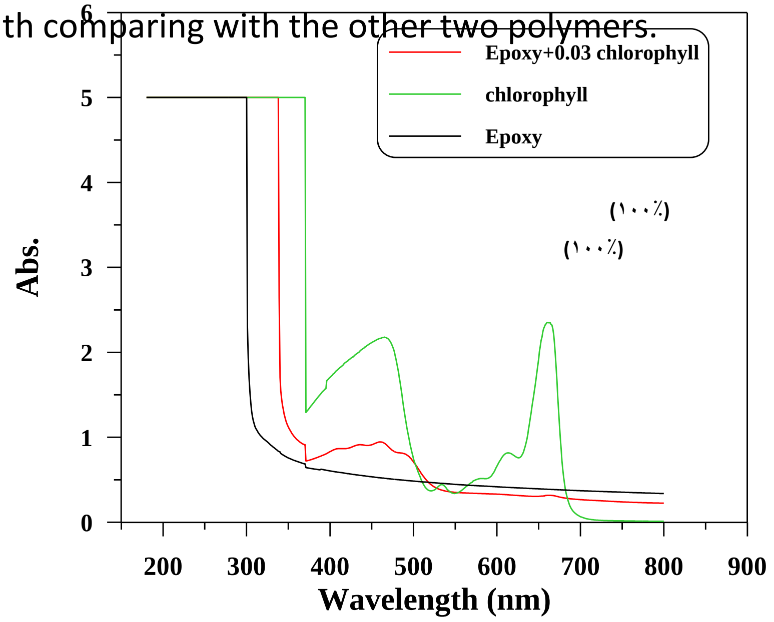


Fig (٤-٣٤): Shows the absorption spectrum of ER.

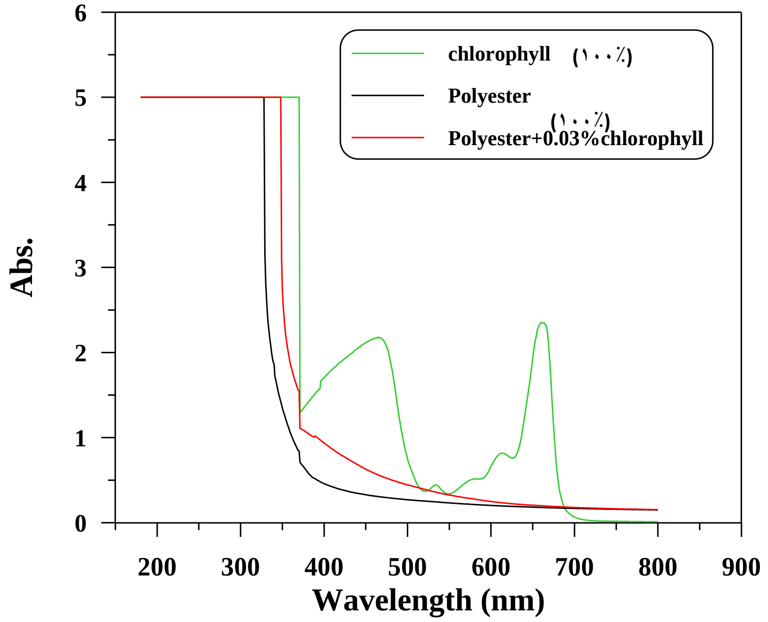


Fig (٤-٣٥): Shows the absorption spectrum of UPE.

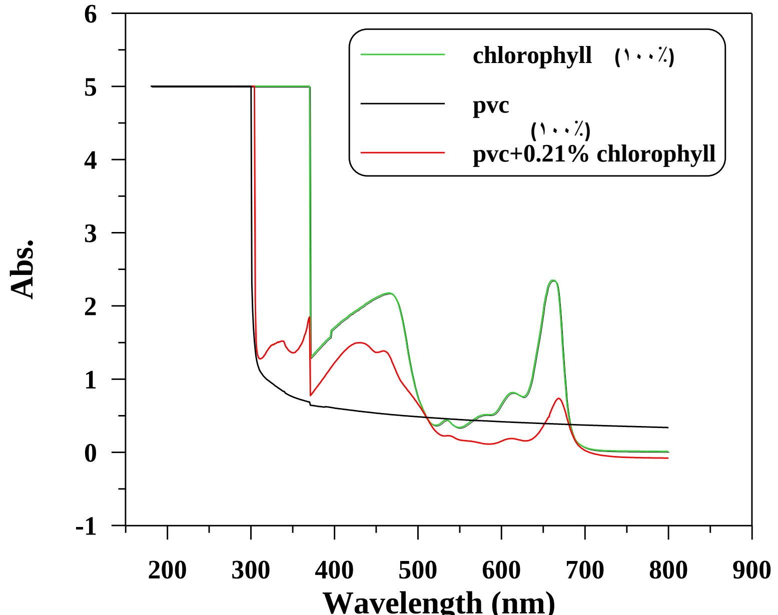


Fig (٤-٣٦): Shows the absorption spectrum of PVC.

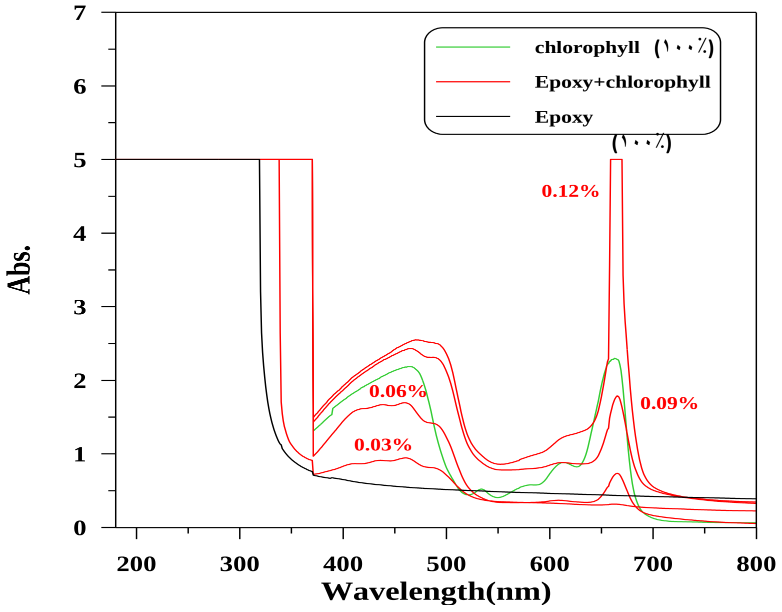


Fig (٤-٣٧): Effect chlorophyll (%) on ER absorption spectrum.

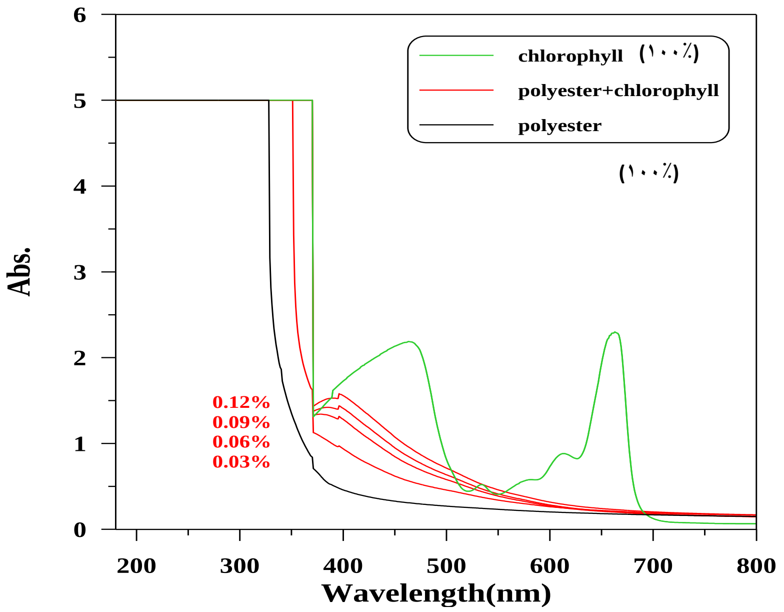
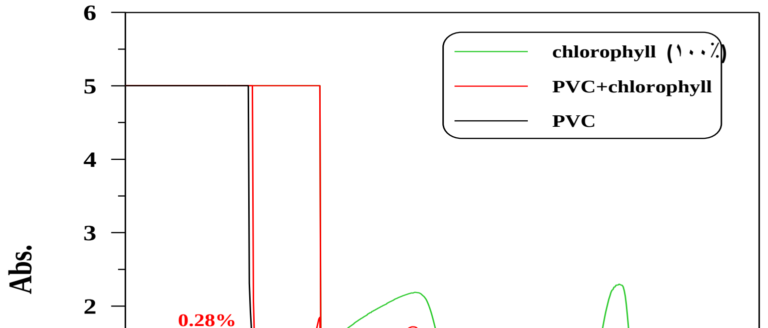


Fig (٤-٣٨): Effect of chlorophyll (%) on UPE absorption spectrum.



(١٠٠٪)

Fig (٤-٣٩): Effect of chlorophyll (%) on PVC absorption spectrum.

As the chlorophyll (chl.) concentration increases result in breaking the interaction sites and extending the neighbored chains in which chlorophyll at these concentrations behaves as plasticizer as the results show (see tables ٤-٢ to ٤-٤).

Table (٤-٢): Bands position of ER.

Band wavelength λ (nm)					
Chlorophyll	Epoxy	ER+٠.٠٣Chl.	ER+٠.٠٦Chl.	ER+٠.٠٩Chl.	ER+٠.١٢Chl.
٤٦٥	٣٨٩	٤٦٠	٤٦٠	٤٦٦	٤٨٤
٥٣٤*		٥٧١		٤٨٦	
٦١٤*					
٦٦٤		٦٦٣	٦٦٦	٦٦٦	٦٧٠

Table (٤-٣): Bands position of UPE.

Band wavelength λ (nm)					
Chlorophyll	Polyester	UPE+٠.٠٣Chl.	UPE+٠.٠٦Chl.	UPE+٠.٠٩Chl.	UPE+٠.١٢Chl.
٤٦٥		٣٨٥	٣٨٨	٣٩٢	٣٩٥
٥٣٤*			٤٢٨	٤٢٨	٤٢٨
٦١٤*					
٦٦٤					

Table (٤-٤): Bands position of PVC.

Band wavelength λ (nm)					
Chlorophyll	PVC	PVC+٠.٠٧Chl.	PVC+٠.١٤Chl.	PVC+٠.٢١Chl.	PVC+٠.٢٨Chl.
		٣٠٣	٣٠٣	٣٣٧	
		٣٧٠	٣٧٠	٣٧٠	
		٤١٧	٤١٨	٤٣٠	
٤٦٥		٤٥٨	٤٥٨	٤٥٩	٤٦١
٥٣٤*			٥٣٧	٥٣٦	٥٣٧
٦١٤*				٦١٢	٦١٢
٦٦٤		٦٦٩	٦٦٩	٦٦٨	٦٦٩

* Low extinction coefficient band.

٤-٦ Effect of pigments addition on the properties of the polymers:

Chlorophyll is added to three polymers (ER, UPE, and PVC) to study the effect of chlorophyll on the mechanical and physical properties on the above three polymers, the tests are:

٤-٦-١ Tensile strength:

Fig (٤-٤٠) shows the relation between the tensile strength and the weight percent of the chlorophyll added. The result shows that an increasing in the tensile strength as the chlorophyll percent increase, such increasing starts to decrease with high percent of chlorophyll. PVC in Fig (٤-٤١) shows decreasing of the tensile strength with very low percent of chlorophyll. As the percent of chlorophyll rises over ٠.١٤٪ tensile strength start to rises until constant value obtained. Tables (٤-٥) and (٤-٦) show the variation of tensile strength with chlorophyll percent.

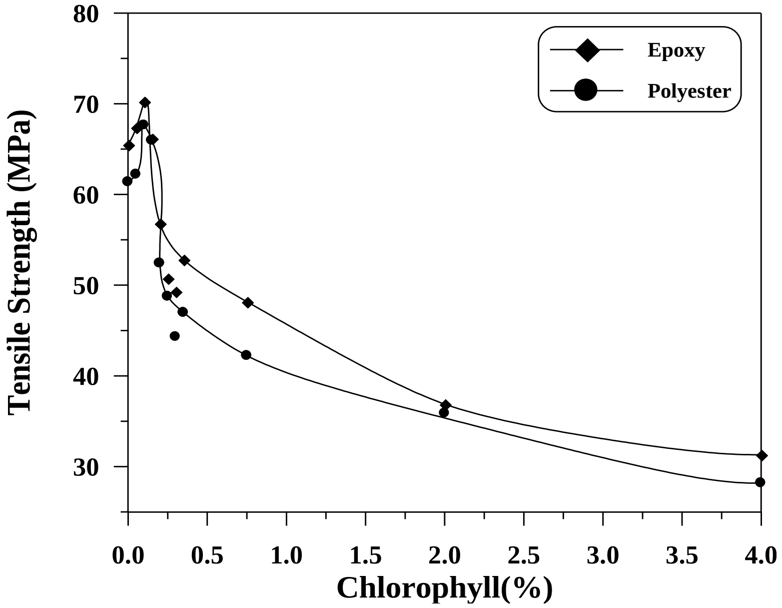


Fig (٤-٤٠): Effect of chlorophyll (%) on tensile strength.

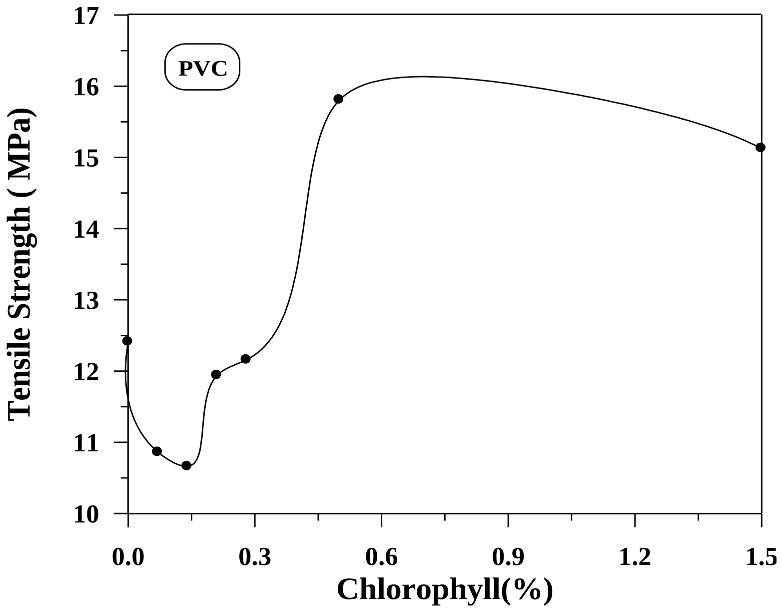


Fig (٤-٤١): Effect of chlorophyll (%) on tensile strength.

Table (٤-٥): The variation of mechanical properties with addition of chlorophyll.

Test	***Chlorophyll (%)***	***Change in mechanical properties (%)***

		ER	*UPE*
Tensile strength	٠.١	↑ ٧.٢٥	↑ ١٠.٢٠
Modulus of elasticity	٠.١	↑ ٢٠.٨٣	↓ ٩.٨٩
Flexure strength	٠.١	↑ ٥.٣١	↓ ٣.٤١
Impact strength	٠.١	↓ ٢٨.٣٩	↓ ٣١.٧٠
	٤	↑ ٢١.٣٢	↑ ٢٦.٦٤
Hardness	٠.١	↑ ١٣.٠٧	↑ ٦.٠٤
	٤	↓ ٣٠.٧١	↓ ٧٩.٨٦

Table (٤-٦): The variation of mechanical properties with addition of chlorophyll on PVC polymers.

Test	***Chlorophyll (%)***	***Change in mechanical properties (%)***	
		PVC	***UPVC***
Tensile strength	٠.٥	↑ ٢٧.٣٧	---
Modulus of elasticity	٠.٥	↑ ١٣.٢٣	---
	١.٥	↑ ٢٨.٧٥	---
Hardness	٠.٥	↓ ٣.١٦	↓ ٦.٧١
	١.٥	↓ ٥.٣٥	↓ ٢٠.١٥
	١٠	---	↓ ٥٠.٣٨

٤-٦-٢ Modulus of elasticity:

Fig (٤-٤٢) shows different behavior between ER and UPE upon the addition of different percent of chlorophyll. With the ER modulus starts to increase as chlorophyll percent increases, until certain value then decreasing as chlorophyll percent increases. While UPE shows decreasing in modulus with chlorophyll percent increase. PVC shows increasing of the modulus with chlorophyll percent increases (see fig ٤-٤٣). The variation of modulus with addition of chlorophyll are shown in Tables (٤-٥) and (٤-٦).

٤-٦-٣ Flexure strength:

Fig (٤-٤٤) shows the ER flexure strength starts increasing with chlorophyll percent increases, to certain value then decreasing as chlorophyll percent increase, while UPE show decreasing flexure strength with chlorophyll percent increase. Table (٤-٥) shows the variation of flexure strength with the addition of chlorophyll.

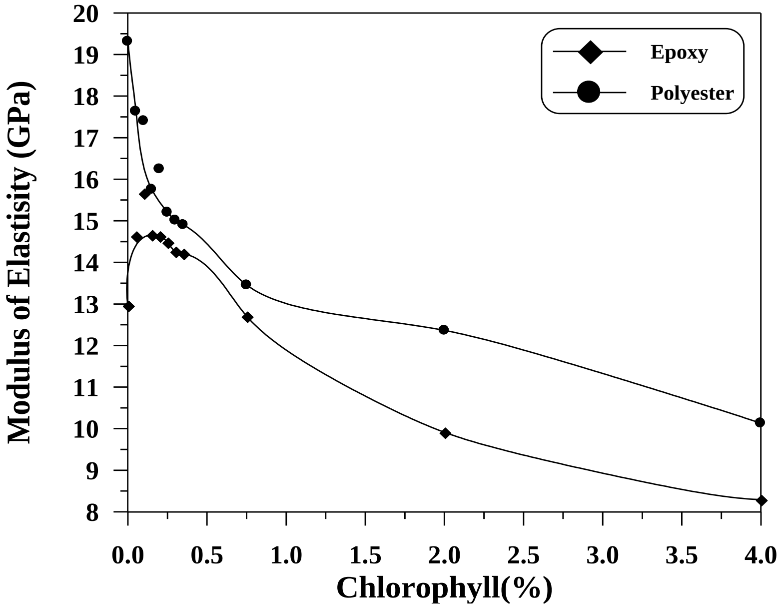


Fig (٤-٤٢): Effect of chlorophyll (%) on modulus of elasticity.

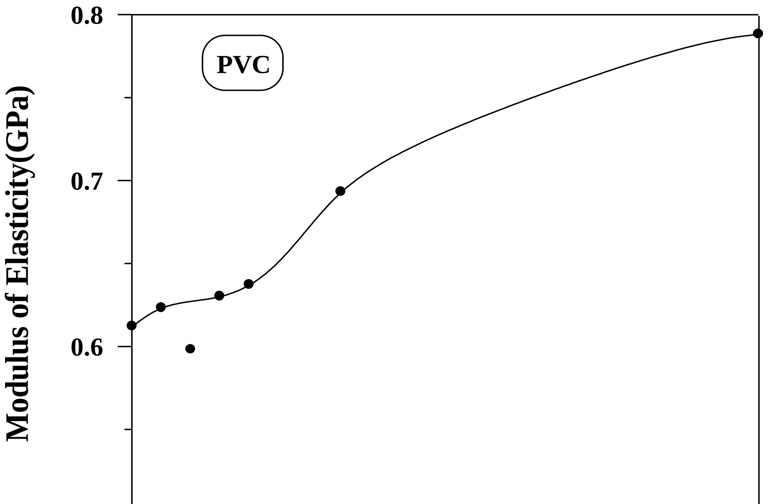


Fig (٤-٤٣): Effect of chlorophyll (%) on modulus of elasticity.

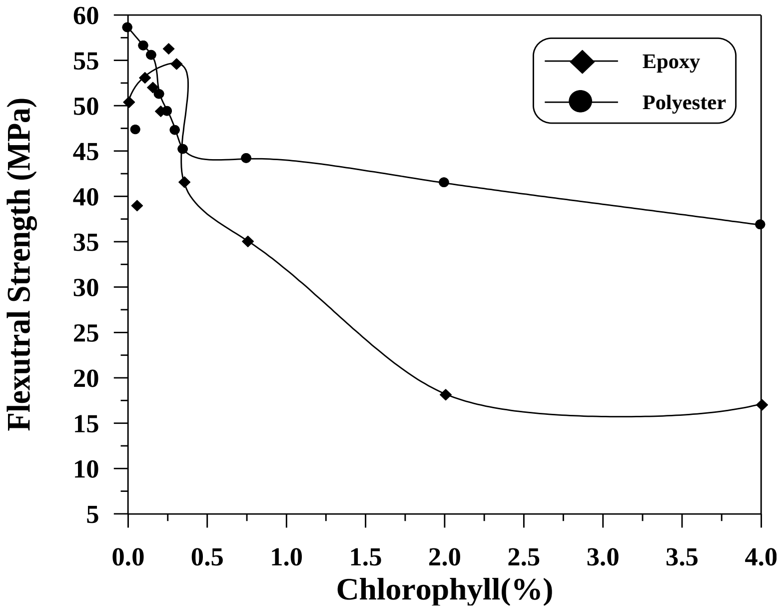


Fig (٤-٤٤): Effect of chlorophyll (%) on flexure strength.

٤-٦-٤ Impact strength:

Fig (٤-٤٥) shows the relation between the impact strength and the weight percent of the chlorophyll. The impact decreases as chlorophyll percent increase, then the impact start increases at high percent of chlorophyll. The variation of impact strength is shown in Table (٤-٥).

٤-٦-٥ Hardness:

Fig (٤-٤٦) shows increasing of hardness in non-linear behavior for ER as chlorophyll percent increases. This behavior inverse at high a percent of chlorophyll. The UPE has similar result as shown in Fig (٤-٤٧). The hardness increases with the increases of chlorophyll percent then starts decrease at a high percent of chlorophyll (see table ٤-٥).

The anthocyanin has similar effects as chlorophyll on ER and UPE hardness, this behavior may be due to that both of them are polar molecules [١٢٠].

In case of β- Carotene pigment the hardness decreases in non-linear behavior with increases the β-caroten percent, which is different behavior from chlorophyll and anthocyanin, which may be due to the less polarity of the former than the later as well as the oily nature of Carotene [١١٥].

The relation between chlorophyll percent and the shore hardness of PVC is shown in Fig (٤-٤٨). The hardness increases with a low percent of chlorophyll, while at a high percent of chlorophyll the hardness starts decreases. This result is similar to the tensile strength and modulus of elasticity data, see Table (٤-٦).Fig (٤-٤٩) shows the relation between chlorophyll percent and the Brinell hardness of UPVC. The hardness decreases with increasing the chlorophyll percent, see Table (٤-٦).

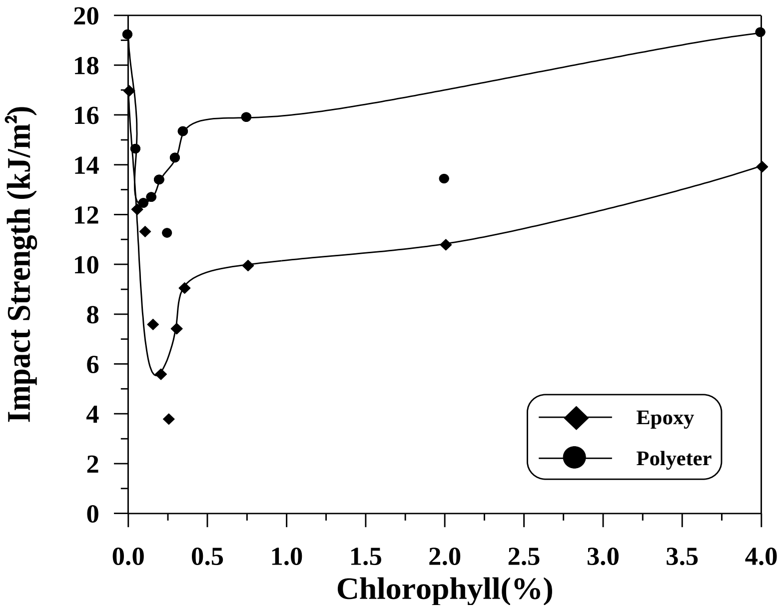


Fig (٤-٤٥): Effect of chlorophyll (%) on impact strength.

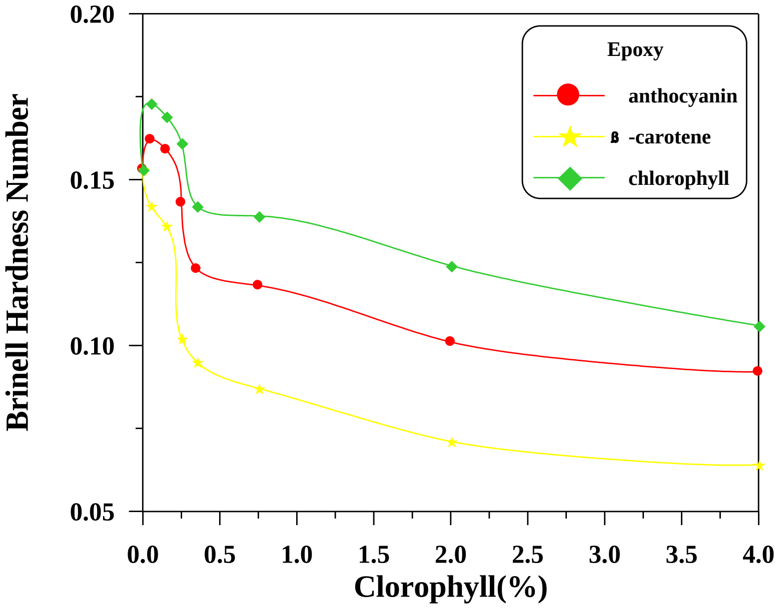


Fig (٤-٤٦): Effect of pigments (%) on hardness.

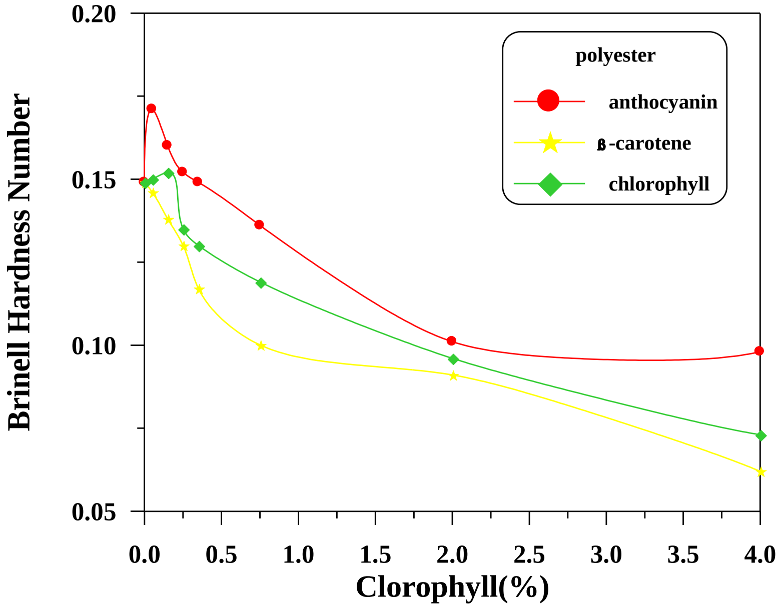


Fig (٤-٤٧): Effect of pigments (%) on hardness.

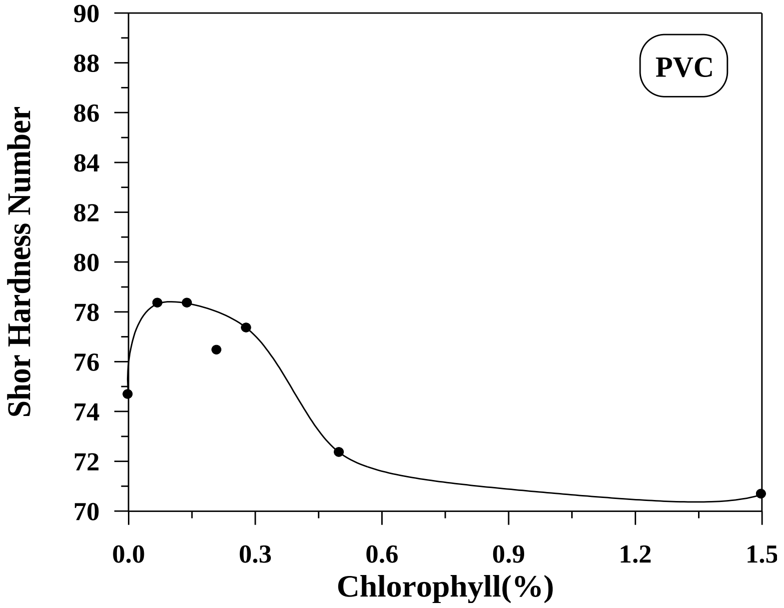


Fig (٤-٤٨): Effect of chlorophyll (%) on shore hardness.

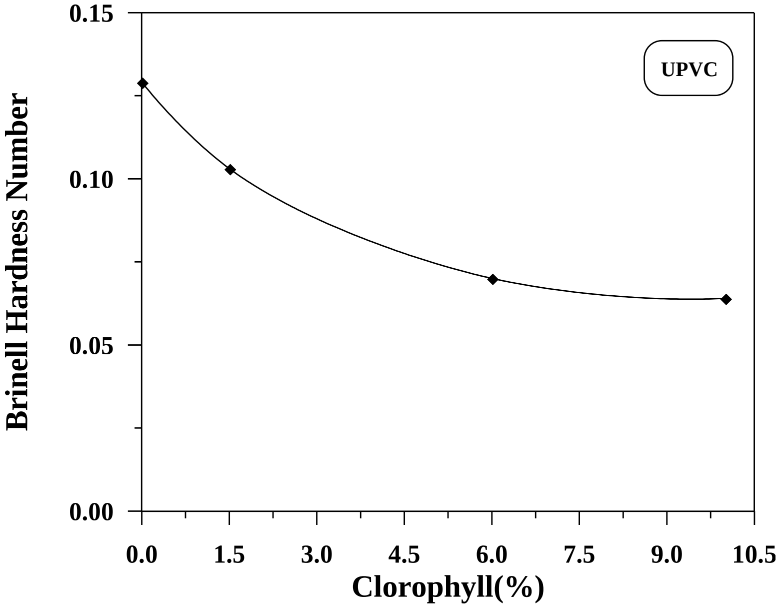


Fig (٤-٤٩): Effect of chlorophyll (%) on hardness.

The above results which represent the effect of chlorophyll addition on mechanical properties can be explained as follow: with a low percent of chlorophyll tensile strength, modulus of elasticity, flexure strength, and hardness increase, this is due to increase cohesive energy between polymers chains, by the physical interaction between polymer chains and pigment, this leads to reduces the ability of the molecule to slide on each others and then rises the mechanical properties, besides that chlorophyll will full inter spaces between the chain, this leads also to support the mechanical properties. This is supported by impact test which decreases in this range of chlorophyll. These results agree with literature [٤٦,٦٥].

In a high percent of chlorophyll (> ٠.٢٪) clear decreasing in mechanical properties except impact appears. This is due to that as chlorophyll increases it behaves as plasticizer which weakening the secondary bond (intermolecular interaction) between the chains comparing with a high percent addition of commercial plasticizer (up to ٥٠٪) to get the same results [٤٦].

From the above results improvement of the toughening and flexibility of brittle polymers (which are used in this project) are obtained by a small quantity of chlorophyll comparing with the high % commercial toughening agents.

Fig (٤-٥٠) shows the effect of chlorophyll on the fractured surfaces results from the impact tests which shows a transition from brittle to ductile fracture.

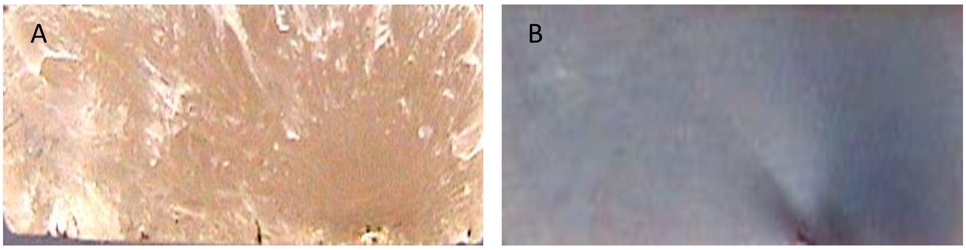


Fig (٤-٥٠): Effect of chlorophyll on fractured surfaces (A- blank sample B- with pigment).

The test shows no significant effect on a specific gravity of polymer by addition of the above pigments.

From the above tests and data obtained we conclude that it is possible to control the physical and mechanical properties of the polymer by added pigment.

٤-٦-٦ Thermal conductivity:

It is noticed from Fig (٤-٥١) that, the thermal conductivity of the polymer increases as the chlorophyll percent increases, this is due to that, vacancies between the polymer chains are filled with chlorophyll as a polar molecules (organo-metallic molecules) [٢١].

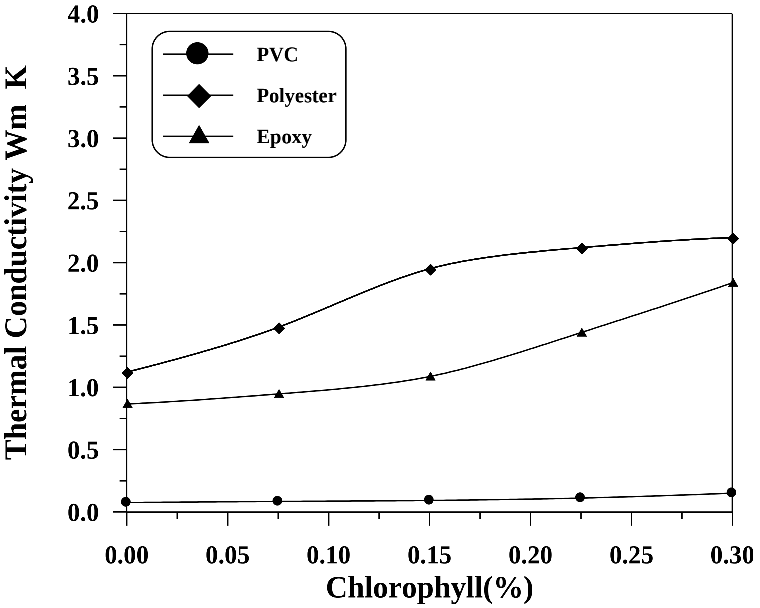


Fig (٤-٥١): Effect of chlorophyll (%) on thermal conductivity.

٤-٧ Effect of heat, UV, and environmental on chlorophyllated polymer properties:

Mechanical tests carried on after exposure sample of polymer with and without chlorophyll to the above conditions to check the ability of chlorophyll to maintain the mechanical properties of chlorophyllated samples.

٤-٧-١ Effect of heat:

Fig (٤-٥٢) to (٤-٥٤) shows the relation between the tensile strength vs heating exposure time for ER, UPE, and PVC.

Fig (٤-٥٥) and (٤-٥٦) show the relation between the flexure strength vs heating exposure time for ER, UPE, and PVC.

Fig (٤-٥٧) to (٤-٥٩) shows the relation between the hardness vs heating exposure time for ER, UPE, and PVC.

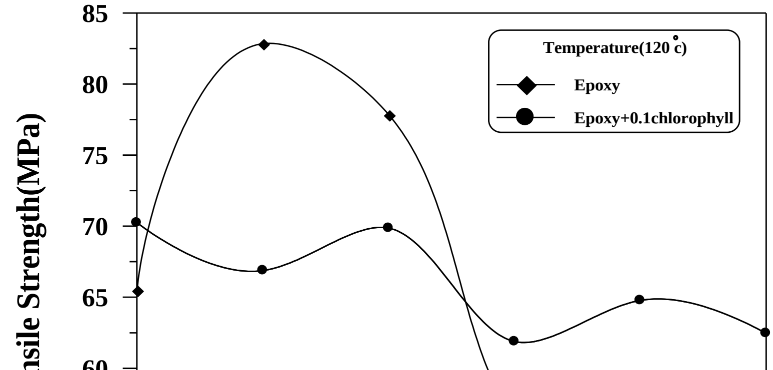


Fig (٤-٥٢): Effect of time exposure on tensile strength at ١٢٠°C.

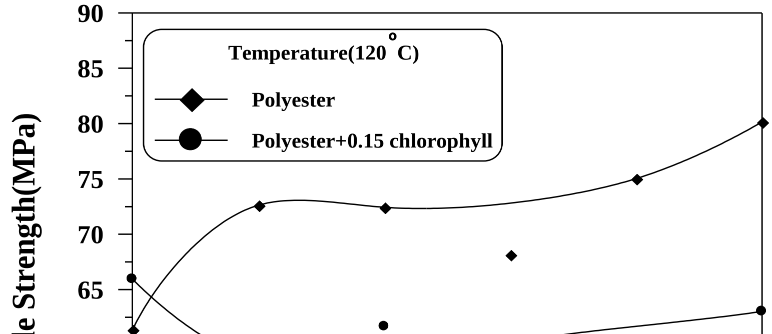


Fig (٤-٥٣): Effect of time exposure on tensile strength at ١٢٠°C.

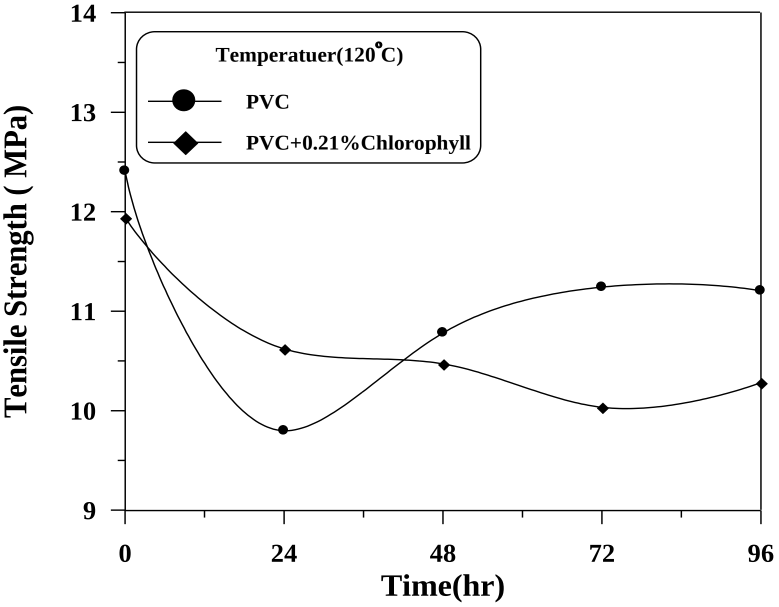


Fig (٤-٥٤): Effect of time exposure on tensile strength at ١٢٠°C.

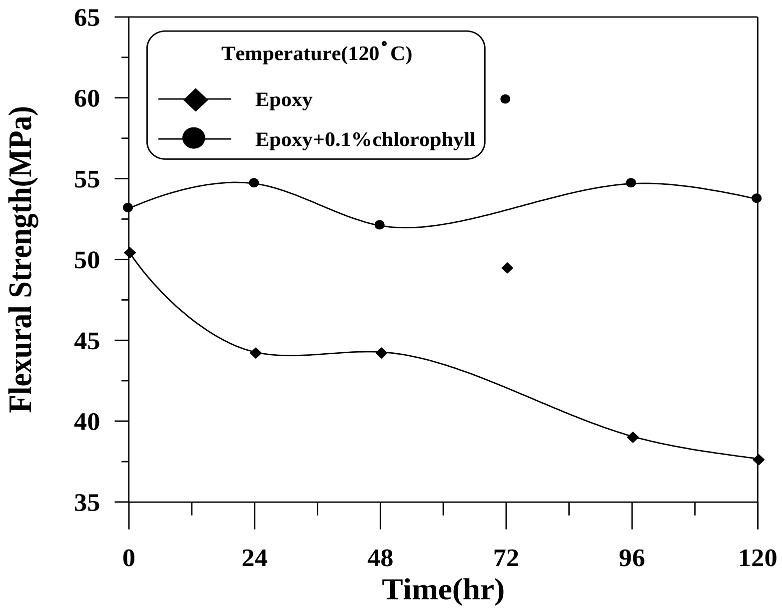


Fig (٤-٥٥): Effect of time exposure on flexure strength at ١٢٠°C.

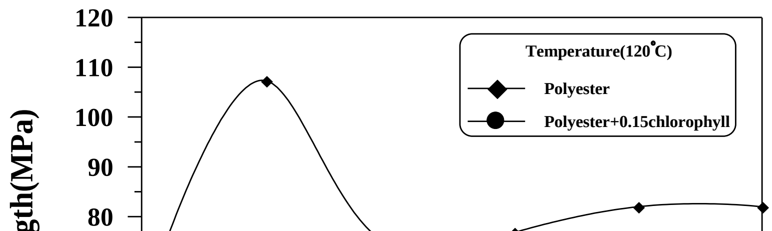


Fig (٤-٥٦): Effect of time exposure on flexure strength at ١٢٠°C.

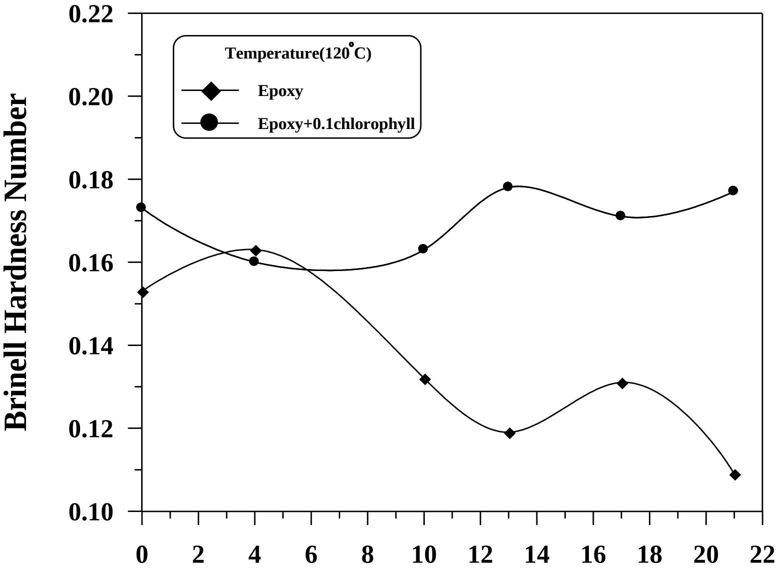


Fig (٤-٥٧): Effect of time exposure on hardness at ١٢٠°C.

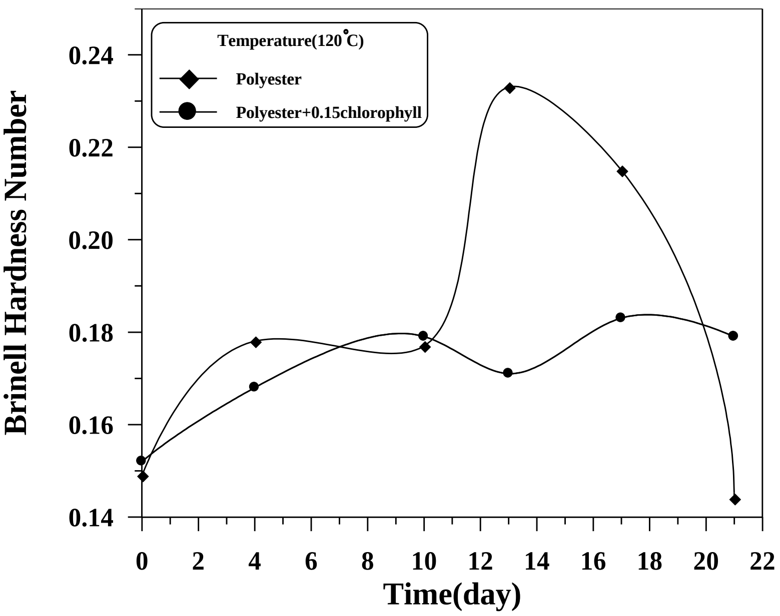


Fig (٤-٥٨): Effect of time exposure on hardness at ١٢٠°C.

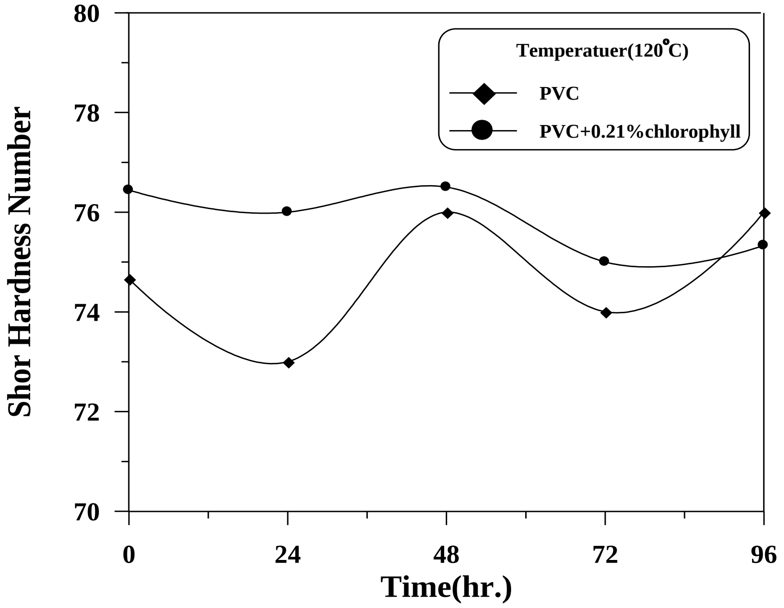


Fig (٤-٥٩): Effect of time exposure on hardness at ١٢٠°C.

٤-٧-٢ Effect of UV – light:

The effects of UV–radiation on polymers hardness are shown in Fig (٤-٦٠) to (٤-٦٢).

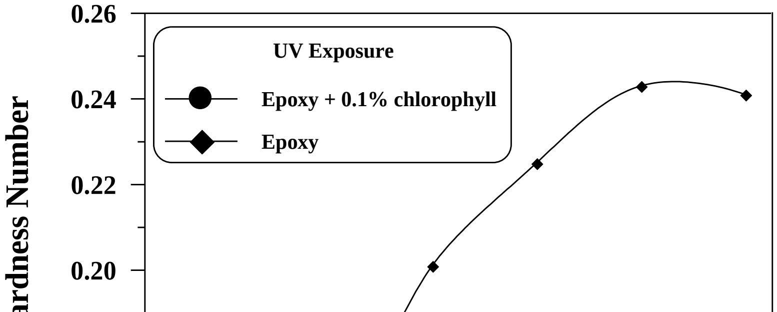


Fig (٤-٦٠): Effect of time exposure to UV on hardness.

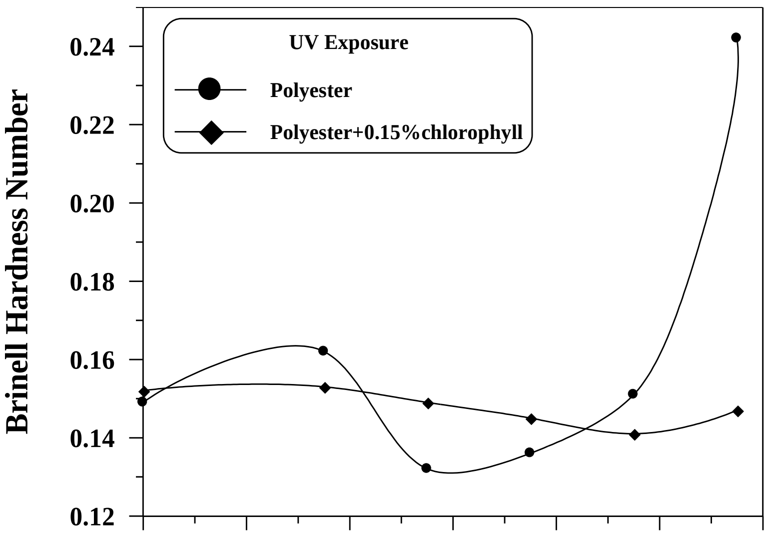


Fig (٤-٦١): Effect of time exposure to UV on hardness.

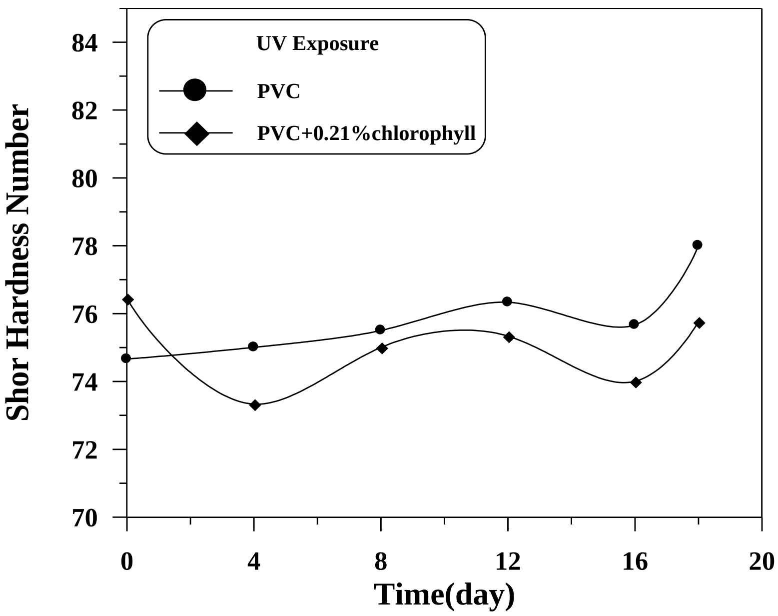


Fig (٤-٦٢): Effect of time exposure to UV on hardness.

٤-٧-٣ Effect of environmental:

Fig (٤-٦٣) and (٤-٦٤) show the relation between the flexure strength vs atmosphere exposure time for ER and UPE.

Fig (٤-٦٥) to (٤-٦٧) shows effect of atmosphere exposure time on polymers hardness (for three used polymers).

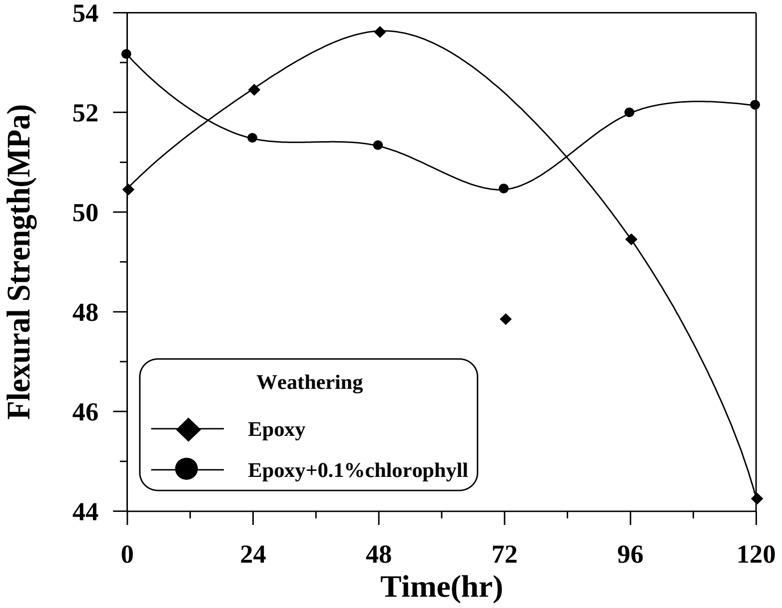


Fig (٤-٦٣): Effect of time exposure to atmosphere on flexure strength.

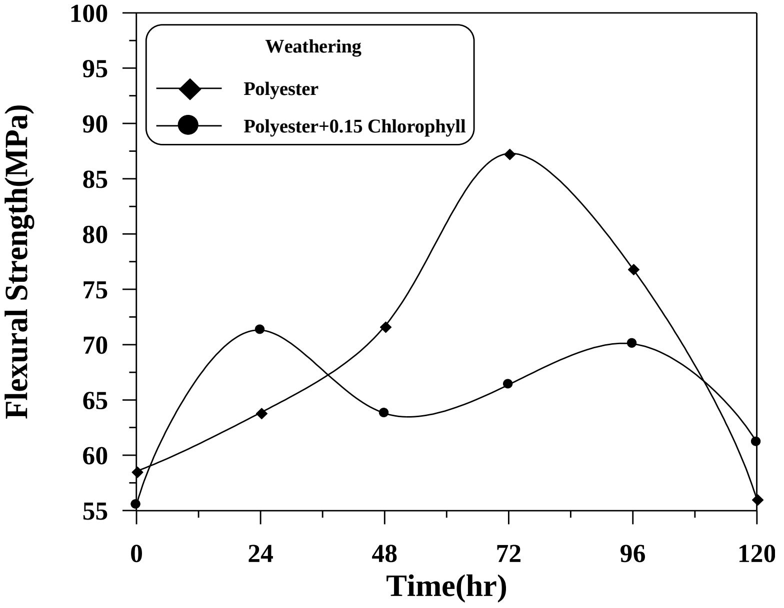


Fig (٤-٦٤): Effect of time exposure to atmosphere on flexure strength.

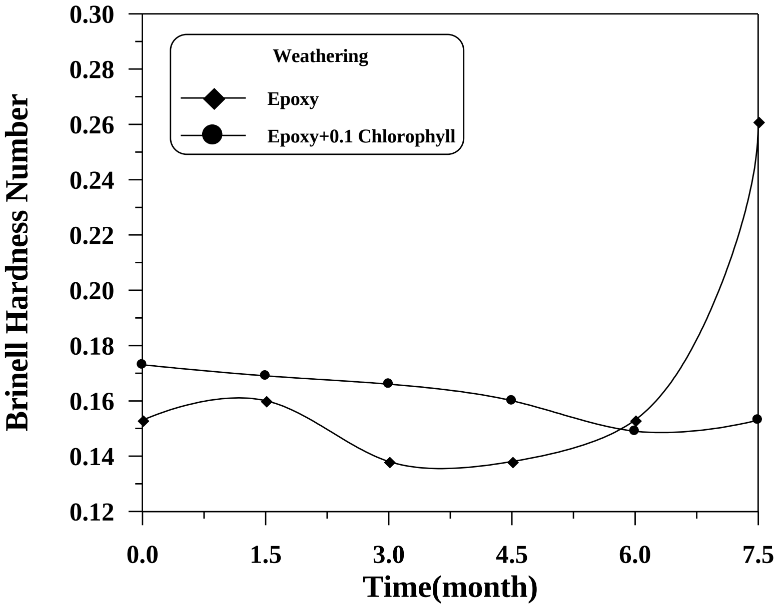


Fig (٤-٦٥): Effect of time exposure to atmosphere on hardness.

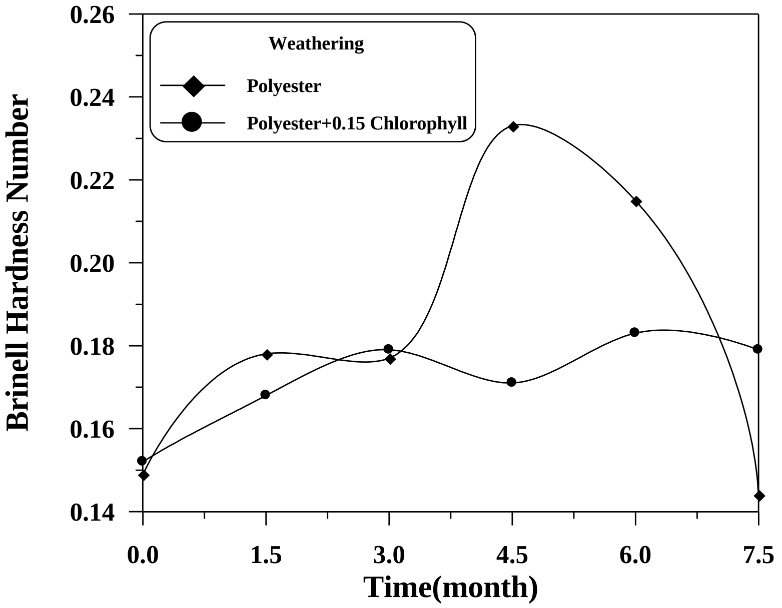


Fig (٤-٦٦): Effect of time exposure to atmosphere on hardness.

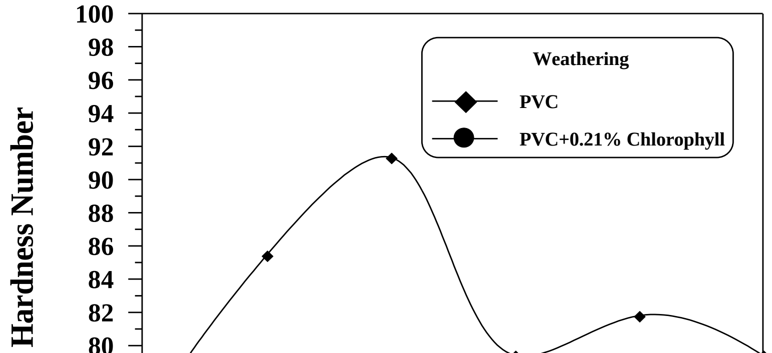


Fig (٤-٦٧): Effect of time exposure to atmosphere on hardness.

These results show that, chlorophyllated samples give regular change against above exposure conditions comparing with irregular change in case of pure polymer, which indicates that, chlorophyll acts as a stabilizer for these polymers against exposure to the above conditions, we conclude for the preceding results that, it is possible to use natural pigments specially chlorophyll which we focus on it in this research as colorant. This widely agrees with that of other workers, who is used the natural pigment in manufacturing of food packaging, packaging material remains almost transparent yet they filter out light in the critical wavelength ranges. They show that, the use of packaging films containing natural coloring pigments slows down the degradation process [٢٨,١٤٠].

Natural pigments also act as stabilizer according to their protection for the polymer from the harmful conditions. The natural pigments have the ability to absorb light in the lower wavelengths of the visible spectrum and in the UV region. Their functions are the protection against the damaging effects of UV light, besides these pigments are considered as antioxidants [١٤١,١٤٢].

All natural pigments used are not poisonous materials, as well as, they are odorless so it is safety materials that used in plastic for all requirement. They are not pollutants as well as they inhibit decomposition of disposal plastic. So these pigments don't have environmentally hazardous or any side effect for human. We avoided commercially synthetic materials, metal oxides, and heavy metals as additives because they are considered as a highly toxic and global pollutants. These artificial additives leach out of the polymer or migrated it over time into air, water, or other substances in which polymer comes in contact, besides that metals don't degrade in the environmental so it resist environmental's break down and have become global pollutants[٣٨,١٣٥].

Finally natural pigments because they are available in a very high quantity and purity as well as regenerated easily from plants, so they will lower the final plastic cost.

Chapter Five

Conclusions and Future Work

٥-١ Conclusions:

١. Natural pigment such as chlorophyll, carotene, and anthocyanin are fit to use as colorant for polymers such as ER, UPE, and PVC.
٢. The coloring samples showed a permanent color even they exposed to heat, UV-radiation, and environmental condition.
٣. The optimum quantity of chlorophyll added to polymers was ٠.١٪, ٠.١٥٪, and ٠.٢١٪ for the ER, UPE, and PVC respectively.
٤. The chlorophyll works as a stabilizers and anti-oxidant for polymers when exposured to heat at ١٢٠ °C in the presents of air:

a- The improvement in the oxidation time for PVC was ٧١.٤٪ relative to the blank sample.

b-The improvement in weight loss was ٢١٢, ١٧, and ٧٪ for the ER, UPE, and PVC respectively comparing with the blank samples.

٥. The chlorophyll has ability to protect polymers against UV-radiation and the improvement in weight loss was ٥١, ٣٥, and ٤٣٪ for the ER, UPE, and PVC respectively comparing with the blank samples.
٦. The environmental stability in weight loss was ٧٩, ٧٣, and ٧٢٪ for the ER, UPE, and PVC respectively comparing with the blank sample.
٧. Interaction between low percent chlorophyll with the polymers molecules appears from the increasing in the tensile, modulus, flexure, and hardness.
٨. In high percent chlorophyll the mechanical properties decreasing while impact increases. In such percent chlorophyll acts as plasticizer by destroying the secondary bond between the polymers chains.
٩. Chlorophyll gives more regular behavior for mechanical properties change of the samples after exposure of these samples to heat, UV-

radiation, and environmental condition. This indicates that chlorophyll acts as advancer against changing condition.

١٠. Due to internal interaction between chain molecules of polymers and chlorophyll molecules, which full the inter spacing between these chain result in improving heat transfer through the polymers.

١١. The best applied chlorophyll percent to the polymer was ٠.٠٣٪ which links in good requirements between mechanical, stabilizer and optical properties agriculture coverers which permit most of the plants required light.

١٢. The presence of the double bond alone (with out other functional group) has no effect on the mechanical properties of the polymers as noted from the result of carotene.

١٣. Chlorophyllated polymers can be used in the medical industry such as syringes and chlorophyll can protect it from x-ray which is used for disinfection.

١٤. Chlorophyllated polymers can be used in drugs and meet packing.

٥-٢ Recommendations for Future Work:

١. One of these pigments (anthocyanin) has many hydroxyl groups in addition to epoxy ring (as present in the epoxy resin). Anthocyanin cans undergo self condensation polymerization with elimination of water molecules. Thus anthocyanin can be used commercially as adhesives materials after polymerization.

٢. Addition of chlorophyll with other plastics materials such as polyethylene to produce color bags this will protect the material inside the bag from the harmful light.

٣. Variation the temperature to study the detail interaction between the pigment and polymer.

٤. Detail study of interaction between anthocyanin and carotene with polymers.

٥. Using these three pigments as antioxidant in rubber industry.

٦. Conducted fatique and torsion tests to gate specific properties such as stiffness/ weight and strength/ weight.

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