PROTECTION OF NATURAL RUBBER FROM ULTRAVIOLET BY USING ANTHOCYANIN PIGMENT

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Mohammed Razzaq Mohammed
Misan University / College of Engineering
m.r.alassadi14@gmail.com

Abstract

Anthocynin pigment is one of natural pigments material. Pigments are present in each one of the organisms in the world, and plants are the principal producers. They are in leaves, fruits, vegetables, and flowers. In this study the effect of anthocyanin pigment on protection of natural rubber from UV radiation and effect of pigment on some mechanical and physical behaviour of natural rubber was assessed. Anthocyanin pigment was prepared from chards by filtration method. It was added to NR from (5pphr) to (25 pphr). The samples with anthocyanin and without were exposed to UV for a various periods and then some mechanical and physical tests were carried out for the prepared specimens. The results showed that the tensile strength, modulus of elasticity, hardness and specific weight decreased with increasing of anthocyanin. Elongation increased with increasing of anthocyanin pigment. When samples exposed to UV, the results showed a broad enhancement in the mechanical properties for all samples contained anthocyanin. This research was used a natural and cheap material available largely in plants to protect of polymers from degradation and to improve their properties instead of synthetics pigments that they are harmful and expensive.

Keywords: Natural Rubber (NR); Anthocyanin; Pigment; Ultraviolet (UV) Mechanical; Physical; Properties.

حماية المطاط الطبيعي من الأشعة فوق البنفسجية باستخدام صبغة الانثوسيانين

محمد رزاق محمد

جامعة ميسان / كلية الهندسة

الخلاصة :

تعتبر صبغة الأنثوسيانين إحدى الصبغات الطبيعية. توجد صبغة الانثوسيانين في كل الكائنات الحية في العالم، وتعتبر النباتات من مصادر الصبغة الرئيسية. توجد الصبغات في الأوراق، الفاكهة، النباتات، والأزهار. تم في هذا البحث معرفة تأثير صبغة الانثوسيانين في حماية المطاط الطبيعي من الأشعة فوق البنفسجية ودراسة تأثير الصبغة على بعض الخواص

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الميكانيكية والفيزيائية للمطاط الطبيعي. حضرت صبغة الانثوسيانين من الشوندر بطريقة الترشيح. وقد أضيفت الصبغة للمطاط الطبيعي من (5 pphr) الى (25pphr) . تم إجراء بعض الاختبارا ت الميكانيكية والفيزيائية للعينات المحضرة المحتوية على الصبغة والغير المحتوية عليها وبعد تعريضها للأشعة فوق البنفسجية لفترات زمنية مختلفة. أظهرت النتائج بان كل من مقاومة الشد، معامل المرونة، الصلادة والوزن النوعي قلت بزيادة نسبة الأنثوسيانين، في حين أن الاستطالة زادت مع زيادة نسبة الإضافة. كذلك بينت النتائج تحسن كبير في الخواص الميكانيكية لكل العينات المحتوية على الانثوسيانين والتي عرضت للأشعة فوق البنفسجية. تم في هذا البحث استخدام مادة طبيعية رخيصة الثمن موجودة بكميات كثيرة في النباتات لحماية البوليمرات من التحلل وكذلك لتحسين خواصها، بدلاً من الصبغات الصناعية التي تكون ضارة وغالية الثمن.

1. Introduction

Fillers and pigments are widely used in polymer materials to provide characteristics to suit a particular commercial application. In many cases fillers can have a marked influence on the thermal and photochemical stability of the polymer material [Norman et al., 2000]. Pigments produce the colors that we observe at each step of our lives, because pigments are present in each one of the organisms in the world, and plants are the principal producers. They are in leaves, fruits, vegetables, and flowers; also, they are present in skin, eyes, and other animal structures; and in bacteria and fungi. Natural and synthetic pigments are used in medicines, foods, clothes, furniture, cosmetics, and in other products [Delgado et al., 2000]. 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 0.01 – 1 µm ranges. 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. As a type of colorant, pigments can be closed as either organic or inorganic, natural or synthetic [Galt et al., 1964] 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 [Harborne et al., 1984]. 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). 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 (1) and (2) show some of inorganic and organic pigments respectively [Cato et al, 2003].

Table (1): Some of the inorganic pigments [Cato et al, 2003].

Pigments	***Chemical Structure***
White	Titanium dioxide TiO_2
Black	Carbon black C
Red	Iron oxide Fe_2O_3
Yellow	Titanium / nickel / antimony oxide
Green	Cobalt / titanium / nickel / zinc oxide
Blue	Cobalt / titanium / chrome oxide
Brown	Chrome / antimony / titanium oxide

Table (2) :Some of the organic pigments [Cato, et al., 2003].

Pigments	***Chemical Structure***
Orange	4 – chloro – 2 - nitroaniline
Red	β – oxynaphthoic acid
Yellow	2 – methoxyaniline
Green	Phthalocyanine
Violet	Quinacridone
Blue	Anthraquinona
Black	Monoazo

Anthocyanins are natural pigments widely distributed in nature. Anthocyanin color molecules are a subclass of flavonoids. They are responsible for the reds, purples, and blues in many flowers, fruits and vegetables. They are found in the petals of petunia, stems of rhubarb, and roots of red radish, for example. Fruits and berries are the most ample sources of anthocyanins in nature. In fruits and berries, anthocyanins are mainly located in the peel, like in apples and grapes, but they are also found in the pulp, as in the case of cherries or blue berries [Maarit, 2005]. Generalized structure for anthocyanin pigments is shown in Fig. (1) [Ronald et al., 2005].

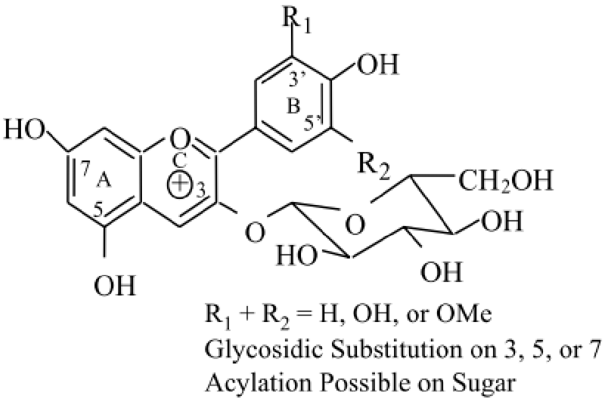

Fig. (1): Generalized structure for anthocyanin pigments. Pelargonidin, R_1 and R_2=H; cyaniding, R_1=OH, R_2=H; delphinidin, R_1 and R_2=OH; peonidin, R_1=OMe and R_2=H; petunidin, R_1=Me and R_2=OH; malvidin, R_1 and R_2=OMe [Ronald et al., 2005].

Using of natural pigments with polymer have been studied earlier [Umoren and Akpablou, 2006, Al-Asadee, 2007, Al- Maamori et al., 2009]. They have demonstrated that the pigments protect the polymers against heat, UV, and environmental effects.

The aim of study is potential of protection of natural rubber from UV by natural pigment that extractor from plants. This pigment that innocuous, easy preparation and cheap, using instead of the harmful and expensive synthetic pigments.

2. Experimental Part

2.1: preparation of the master batch

The master batch was comprised of natural rubber and some additives that were used according to international standard. The table (3) was showed the used recipe.

Table (3): Ingredient of the used recipe without additives [Robert, 1987].

Compounding ingredients	pphr
Natural Rubber	100
Streaic Acid	2
Zinc Oxide	5
MBTS	1
Sulfur	2.75

The streaic acid and zinc oxide were used as activating material , MBTS (2,2-Dibenzothiazyl disulphide) was as accelerating material, while sulfur was used as vulcanizing material.

The mixing was carried out by laboratory mill (Comerio Ercole Busto Avsio , Italian's made), rolls dimensions were: outside (150mm), working distance (300mm), speed of the slow roll (24 rpm) and gear ratio (1.4). The roll mill had the facility of controlling the gab distance between the rolls and the rolls temperatures. The program of mixing and homogenizing were carried out according to the following steps :

1) Passing rubbers through rolls several times with decreasing a mill roll opening to 0.2 cm, at 70°C.
2) The stearic acid, zinc oxide, MBTS and sulfur were added respectively to rubber between rolls with the continuous mixing.
3) After the master batch was completed, the anthocyanin pigment was added to rubber according to sample.
4) The composite material was rolled continuously with decreasing a mill roll opening for final homogenized.
5) The composite material was cooled at room temperature.

2-2. Anthocyanin:

The Chards gives a better result than other plants, so, the anthocyanins content extracted from it by water. First cutting the chard root into thin slices and mixing them with water for 24 hours, then filtering the solution by cotton cloth and stored it in order to be used.

2-3 Samples Preparation:

2-3-1 Samples preparation of the tensile test:

The tensile samples were prepared by using laboratory mill. Take the materials from the mill as a sheet. A hydraulic press was used to homogenize the sheet thickness and to complete the vulcanization. The sample was pressed under pressure equaled (200 psi) at (145 °C) for (45 min). The sheet pressed with mould consists of two parts each of them in the dimensions of test sample, the part dimension (200×200×5) mm. Two samples were cut from the sheet. The cutting was made by using hand press type Wallace Test Equipment.

Tensile properties were determined according to ASTM-D412 by using the Monsanto Tensometer T10. Dumbbell-shaped specimens were conditioned at room temperature. A cross head speed of 50 mm min^{-1} was used. The average of three samples was used during the test.

This testing equipment was controlled by a microprocessor together with a plotter and pneumatic sample holder. It is designed for testing tensile strength, modulus of elasticity and elongation percentage at break, this microprocessor together with a plotter and pneumatic sample holder assists in obtaining a written record of each test more independent of the operator, who supplies dimensional and identification information and fits the test piece in the testing equipment before starting the test. This gives improved consistency compared with manual methods of measuring extension and mechanical methods of measuring loads.

2-3-2 Samples preparation of the hardness, resilience and specific gravity

The samples were prepared as following steps:

1. Preheating for molds at 150°C, the mold had dimensions (length, width, thickness) (200,180, 6.5) mm respectively, the mould had nine circler disk equality in volume, the disk diameter was (45 mm), and it's thickness was (3 mm).
2. The recipe was putted in mold which putted under hydraulic press, the used pressure (200 psi) and temperature (150°C) for (30 min) to complete the vulcanization.
3. The samples were existed from the mold and remained for 24 hours for cooling before the test operation.

The International Hardness test is used in measurement of the penetration of rigid ball into the rubber specimen under specified conditions. The measured penetration is converted to the International Rubber Hardness Degrees (IRHD).

Wallace Dead Load Hardness Testers was used to test of hardness samples according to ASTM D-1415.

Determination of specific gravity yields for Archimedes base which states that the apparent loss in weight of a body immersed in a liquid equal to the weight of the liquid displaced [Craig, 1963].When the weight of the body and the weight of equal volume of water is known, therefore the specific gravity can be determined which is, by the definition, the ratio of.

Weight of a given vol. of body/Weight of equal vol. of water

Thus, S.G = [Wt. of body in air/(Wt. in air–Wt. in water)] * S.G of liquid

Monsanto-Densitorn was used to test of specific gravity samples.

Wallace R2-Dunlop Tripsometer takes the form of an out of balance metal disc revolving on virtually frictionless bearing and which acts as a slow moving pendulum. The test piece is placed against a rigid support so that it receives a blow at its center. A circular scale is provided for measuring the angle of displacement .The measured quantity is the angle to which the disk rebounds after the hammer strikes the specimen. Tests are carried out according to ASTM D1054.

Samples of tensile, hardness, resilience and specific gravity tests were exposed to UV-radiation according to (ASTM-D-1148-70) from UV source (Oviel Corporation) works on 16 watt (380 kJ mol -1) and wave length 375-380 nm.

3. Result and Discussion:

3.1 Tensile Strength and Modulus of Elasticity:

Figures (1) and (2) show the effect of pigment percent on the tensile strength and modulus of elasticity of NR. It can be seen that the tensile strength and modulus of elasticity for the composites slump with increasing pigment percent. This behaviour may be attribute to work of the anthocyanin pigment as plasticizer, that lead to weak the intermolecular interaction forces so, the rubber chains slide one to another therefore tensile strength and modulus of elasticity decreased. when samples were subjected to UV for two weeks, a slight improvement feature of tensile strength and modulus of elasticity happened compared to the corresponding value in case of absence of exposure to UV radiation, this is due to create the free radicals in the rubber chain by UV which break some bonds near the surface, and work these roots to form a few percent of cross links between rubber chains, causing improvement in tensile strength and modulus of elasticity. But when samples were subjected to UV for a longer period and a result of the large number of entanglements lead to contraction of sample and generating of cracks, these cracks are superabounding with increasing duration of exposure to UV, the tensile strength and modulus of elasticity were reduced, but we note that the rate of decreasing of tensile strength and modulus of elasticity for the samples with anthocyanin pigment was slightly compared with samples not contained anthocyanin, this gives a clear result on the anthocyanin pigment protection of rubber from the degradation by UV because of it absorbed radiation.

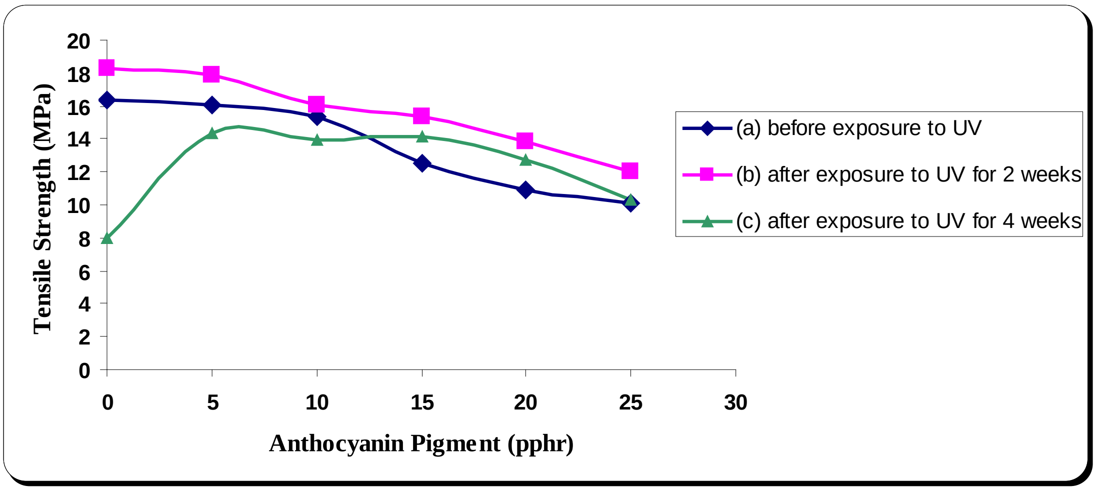

Fig. (1): Effect of anthocyanin pigment on tensile strength of natural rubber: (a) before exposure to UV, (b) after exposure to UV for 2 weeks, (c) after exposure to UV for 4 weeks.

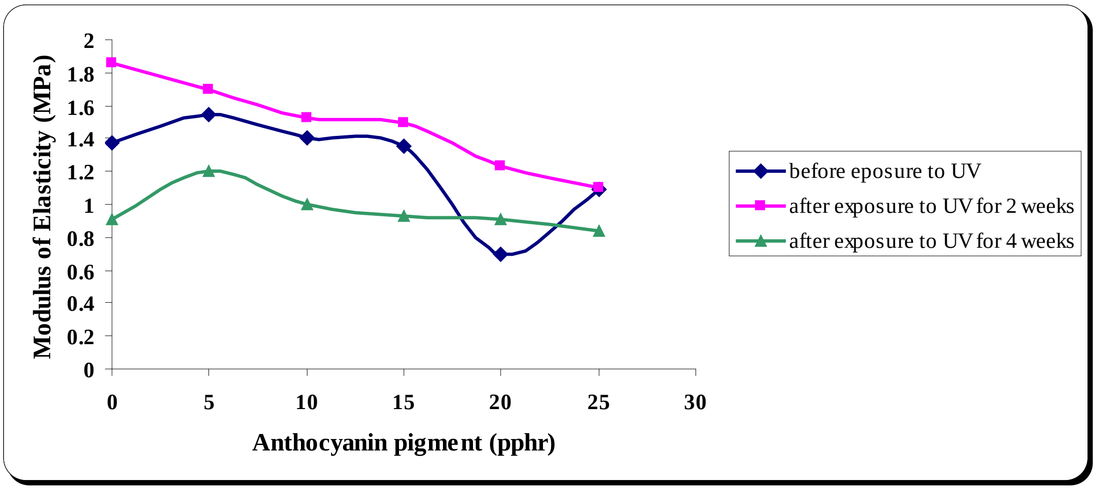

Fig. (2): Effect of anthocyanin pigment on modulus of elasticity of natural rubber: (a) before exposure to UV, (b) after exposure to UV for 2 weeks, (c) after exposure to UV for 4 weeks.

3.2 Elongation

Figure (3) shows the effect of pigment percent on elongation of NR. It can be seen that the elongation for the composite jumps with increasing pigment percent. At loading apply, the chains slide easily due to the pigment, this is lead to increase elongation. At exposure to UV, the sample becomes brittle due to entanglements, so the chains become unable to move, therefore, the elongation is decreased.

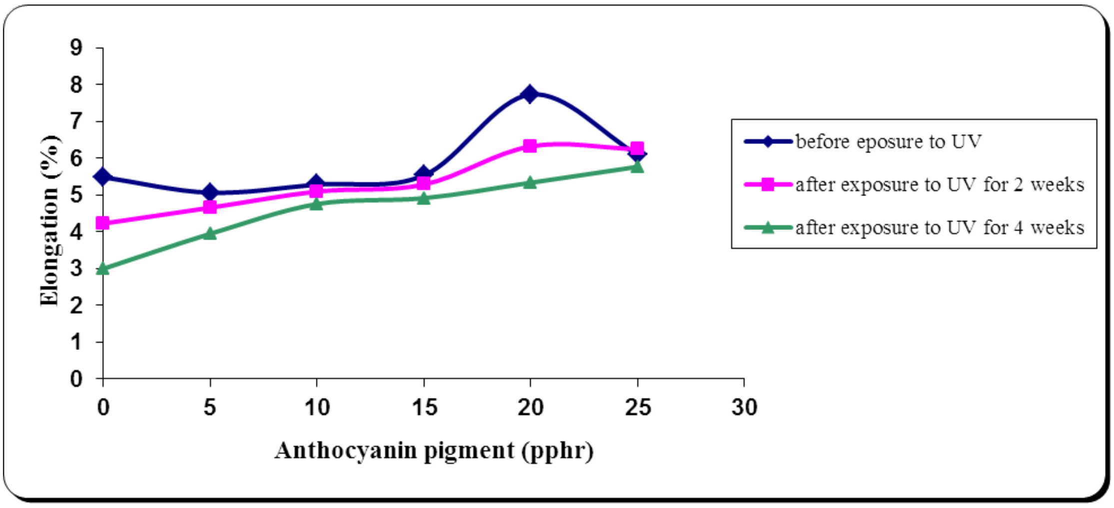

Fig. (3): Effect of anthocyanin pigment on elongation of natural rubber: (a) before exposure to UV, (b) after exposure to UV for 2 weeks, (c) after exposure to UV for 4 weeks.

3.3 Hardness

Figure (4) shows the effect of pigment percent on hardness of NR. It can be seen that the hardness of the composites decreases with increasing pigment percent. This behaviour may be attribute to the penetration of the anthocyanin molecules among the rubber chains lead to weakness of intermolecular interaction forces for the rubber chains so, the requisite load to penetrate or scrat of the sample was decreased. But, when compared between the sample contained pigment and the sample without pigment, we note a large increment of hardness for sample without pigment after exposure to UV because of increasing of crosslinks which happened due to UV, this improve that the anthocyanin pigment works as stabilizer.

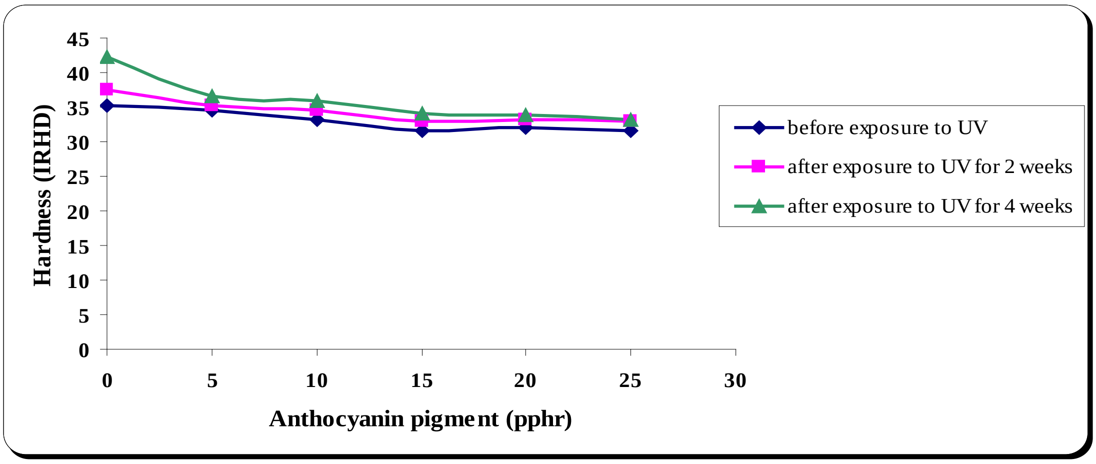

Fig. (4): Effect of anthocyanin pigment on hardness of natural rubber: (a) before exposure to UV, (b) after exposure to UV for 2 weeks, (c) after exposure to UV for 4 weeks.

3.4 Resilience

Figure (5) shows the effect of pigment percent on the resilience of NR. It can be seen that the resilience plummets with increasing pigment percent. This behaviour may be attributing to anthocyanin pigment acts as plastizer that interact between rubber chains and decrease the interaction molecular forces thus the resilience decreased.

From same figure, it can be seen that the resilience increases at exposure to UV due to increasing of cross-links by free radical which happened by UV, these cross-links are astriction the chains movement, thus increasing of the resilience.

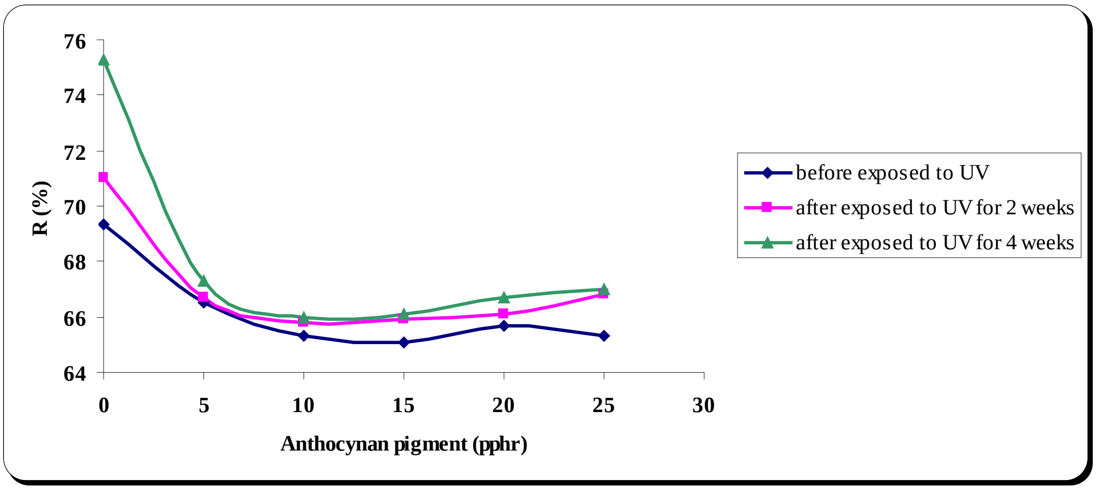

Fig. (5): Effect of anthocyanin pigment on resilience of natural rubber: (a) before exposure to UV, (b) after exposure to UV for 2 weeks, (c) after exposure to UV for 4 weeks.

3.5. Specific gravity

Figure (6) shows that the addition of anthocynin pigment to (NR) leads to reduction in the specific gravity, this behaviour may be attribute to work the anthocynin molecules as a plastizer and they penetration among the rubber chains that lead to weakness of intermolecular interaction forces for the rubber chains. As well as the big molecules for anthocynin serve to create the voids among the chains, also the anthocynan pigment contained water, during molded the water was evaporated leaver other voids which leads to reduction the weight to volume unit. lastly, the specific gravity of anthocynan pigment lower than of rubber, so the specific gravity reduced. From same figure, it can be seen that the specific gravity decrease when samples exposed to UV compared with the absence of exposure to ultraviolet. The radiation breaks some bonds and forms free radicals and entanglements which lead to liberation gas and lose of weight for the sample per unit volume, and also due to the proportion of a large entanglements formed by UV will happen shrinkage of sample that lead to the creation of cracks in the sample increases with increasing duration of exposure to UV, where these cracks work on reduce of density, therefore; decreasing of specific gravity. With respect to the samples without pigment, we note a substantial decreasing in specific gravity after exposure to UV for two and four weeks compared to the samples contained the pigment. the anthocyanin pigment absorb the UV radiation and turn it into a harmless thermal energy, these results are consistent with the results of other researchers [Al-Asadee, 2007; Al-Maamori et al., 2009].

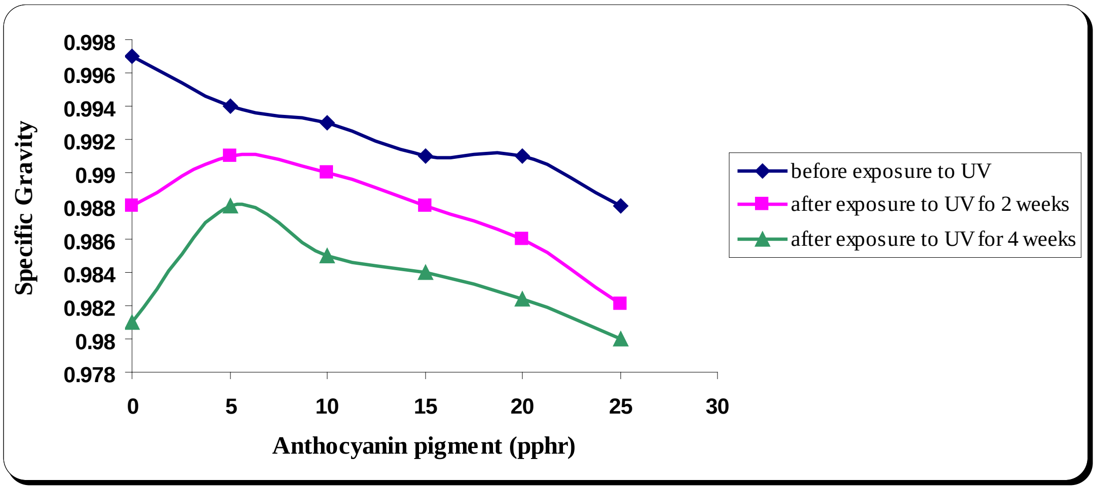

Fig. (6): Effect of anthocyanin pigment on specific gravity of natural rubber: (a) before exposure to UV, (b) after exposure to UV for 2 weeks, (c) after exposure to UV for 4 weeks.

4- Conclusion

Experiments were performed in order to determine the effect of anthocyanin pigment on mechanical and physical behaviour of natural rubber and use of natural additives to protect the rubber from degradation instead of synthetic materials which harmful to human and to environment. The results obtained from the use of anthocyanin pigment are as follows:

- Tensile strength, modulus of elasticity, hardness, resilience, and specific gravity decline with increasing of pigment.
- Pigment improves ductility and lead to reduce the brittle failure.

- Presence of anthocyanin pigment in rubber has played as a plastizer and leads to weak of intermolecular interaction forces for the rubber chains then the result material becomes elastic and plastic and it may be used in a large engineering applications, for example in an athletic applications.

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