Effect of chlorophyll and anthocyanin on the secondary bonds of poly vinyl chloride (PVC)

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Abstract: This paper deals with the effect of natural pigments (chlorophyll and anthocyanin) on the secondary bonds in (poly vinyl chloride PVC), which play an important role in the physical and chemical behavior of it. Natural pigments extracted from plants by a simple method and blended with PVC powder in different ratio of natural pigments, and the properties of the blend were determined and compared. The extracted pigments were characterized by UV- visible spectroscopy and Fourier transform infrared spectroscopy (FTIR). The blend of PVC with pigments were characterized by FTIR, differential scanning calorimetry (DSC), hardness, and density. The results show that anthocyanin shows higher depression in glass transition temperature (T_g) of PVC than chlorophyll pigment, where the maximum effect of chlorophyll is 3%. The obtained T_g used in calculations depending on molecular models which its content the simplest idealized model of a linear molecule is the chain model without branching. The hardness and density of PVC decrease as anthocyanin and chlorophyll percent increases. All these results were contributed to that chlorophyll and anthocyanin act as plasticizers by effecting on secondary bonds of PVC polymer.

Keywords: Poly Vinyl Chloride (PVC), Natural Pigment, Secondary Bonds, Glass Transition Temperature (T_g)

1. Introduction

Even when all the primary valences within covalent molecules are saturated, there are still forces acting between the molecules. These are generally known as secondary valence or intermolecular forces, or van der Waals forces. The following three types are recognized, and the first and third in particular contribute greatly to the physical properties of polymers.Dipole forces, when different atoms in a molecule carry equal and opposite electric charges, the molecule is said to be polar or to have a dipole moment. Induction forces, a polar molecule also influences surrounding molecules that do not have permanent dipoles. The electric field associated with a dipole causes slight displacements of the electrons and nuclei of surrounding molecules, which lead to induced dipoles.Dispersion forces, the existence of intermolecular forces in nonpolar materials, plus the small temperature dependence of intermolecular forces even where the dipole effect is known to far outweigh the induction effect, suggests the presence of a third type of intermolecular force. The bond in which a hydrogen atom is associated with two other atoms is particularly important in many polymers, including proteins, and is held by many to be essential to life processes. Since the classical concepts of chemical bonding allow hydrogen to form only one covalent bond, the hydrogen bond can be considered electrostatic or ionic in character [1].

Acid – Base interaction:

1. Exothermic reaction (chemical reaction that releases energy in the form of light or heat. It is the opposite of an endothermic reaction).
2. No need to change backbone structure.
3. Careful selection of surface treatment method, adhesive and solvent.
4. Acidity and basicity can be measured by Fourier-transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS), Calorimetry (see table 1)[2].

PVC is a thermoplastic polymer that can be processed by a variety of techniques like injection molding, extrusion, blow molding, and compression molding. PVC is an amorphous, rigid polymer due to the large side group (Cl, chloride) with a T_g of 75 to 105ºC and softens at about 85°C. Also in rubbers,

PVC are sometimes added in order to improve the impact strength. It is fairly weak and extermely notch-sensitive but has excellent resistance to chemicals. PVC structure shows in fig. 1[3-5].

Table 1. Typical primary-Bond Energies (Acid -Base Interaction)[2].

Bond Type	Bond Energy (kJ mol^{-1})
Primary bonds	
Ionic	600 - 1100
Covalent	60 - 700
Metallic	110 - 350
Donor -acceptor bonds	
Bronsted acid - base interactions	Up to 1000
Lewis acid - base interaction	Up to 80
Secondary bonds	
Hydrogen bonds Involving fluorine	Up to 40
excluding fluorine	10 - 25
Van der Waals bonds	
Permanent dipole–dipole interactions	4 - 20
Dipole-induced dipole interactions	< 2
Dispersion(London) forces	0.08 - 40

Plastic additives are a diverse group of specialty chemicals that are either incorporated into the plastic product prior to or during processing, or applied to the surface of the product when processing has been completed[6].

Plasticizers are large organic molecule additives of low volatility that are added to plastic compounds to improve their flexibility, extensibility, and processability. They increase flow and thermoplasticity of plastic materials by decreasing viscosity of polymer melts, glass transition temperature (T_g), melting temperature (T_m), and elasticity modulus of finished products[7].

Most would agree that any material which can be added or applied to a substrate to give it color may be referred to as a colorant and the process of addition or application can be referred to as coloration or simply coloring[8].Colorants are generally classified as inorganic or organic materials. Generally, inorganic colorant are coarser particles of lower coloring efficiency, stable to heat, light, and chemical environment, and less expensive per kilogram (kg). But many of the brightest colors are made from metals or their compounds whose toxicity is causing health concerns, both in manufacturing and in the ultimate environment. Organic colors are finer particles of higher coloring efficiency, less stable, and more expensive per kg (although not necessarily in the low concentrations required to produce the desired color); they are generally nontoxic. Colorants may also be classified as dyes or pigments[9].

Dyes are highly colored, aromatic-organic molecules. anions or cations of modest size, with relative molecular masses(rmm) ranging from as low as 200 to significantly more than 1000. Dyes are soluble at the molecular level in the media where they are applied. See (fig. 2)[8, 10, 11].

Pigments are particles, usually with a size in the 0.01 - 1 μm range. The particle size is one of several parameters of technical importance for the pigment products. Pigments may be white as well as colored; contrast this with dyes. There are p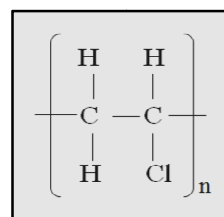igments which are entirely aromatic-organic or organo-metallic co-ordination compounds. Pigments are virtually insoluble[8, 11].

When the dye is dissolved in a solvent, every chromogen is available to absorb light, and the solution is clear. Other advantages of dyes are their solubility and non-abrasiveness. However migration, sublimation, solid nature, price, and the toxicity of dyes can be a concern. By contrast, the same concentration of a pigment dispersion absorbs less light than that of the dye since many of the pigment chromophores are "in the shadow" of other chromophores[12].
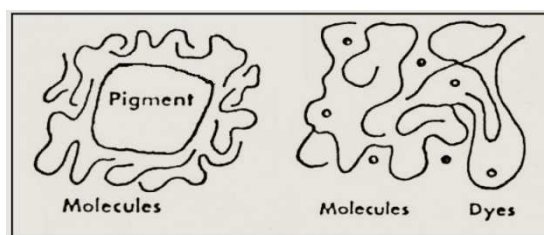
Plant pigmentation is generated by the electronic structure of the pigment interacting with sunlight to alter the wavelengths that are either transmitted or reflected by the plant tissue. Chlorophyll with peak absorbencies at 430 and 680 nm will leave wavelengths forming a green colour. Of course, often the colours are the result of a mix of residual wavelengths; for example, anthocyanins absorbing yellow-green light wavelengths of 520–530 nm will generate mauve colours formed by the reflection of a mix of orange, red and blue wavelengths[13].

Chlorophylls are the pigments that make plants green and are arguably the most important compounds on earth as they are required for the harvesting and transduction of light energy in photosynthesis. The largest proportion of light energy absorbed and transduced in photosynthesis is by direct absorption of light by chlorophylls. Chlorophyll a and chlorophyll b are the major types of chlorophylls found in plants[13].

Anthocyanins are the most abundant and widespread of the flavonoid pigments. They absorb light at the longest wavelengths, and are the basis for most orange, pink, red, magenta, purple, blue and blue-black floral colours. Key to providing such colour diversity is the degree of oxygenation of the anthocyanidins (the central chromophores of the anthocyanins) and the nature and number of substituents (e.g. sugar moieties) added to these chromophores. An important characteristic of anthocyanins is that they undergo pH-dependent changes in colour intensity and hue or even loss of colour[13].

Fig. 1. PVC Structure[4].

Fig. 2. Mechanism of coloration[10].

2. Experimental Procedures

2.1. Materials

Poly (vinyl chloride) (PVC) powder was obtained from Yonghui chemical Holdings Limited Company, china. Chlorophyll extracted from Iraqi citrus aurantium leaves, anthocyanins extracted from cherry fruit imported from Iran, ethanol, and distill water.

2.2. Extraction of Natural Pigment

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 porphyrinnucleus[14].Here, chlorophyll extracted from citrus aurantium leaves by ethanol by cleaning the citrus aurantium leaves by distill waterthen dried at temperature 25°C. Cutting the dry citrus aurantium leaves to smaller pieces to facilitate the extraction process due to increasing the surface area exposed to the solvent. Then immersing in ethanol in amount that covered all the leaves covered the beaker to inhibit the evaporation of the solvent. After 5 days remove the remnants of extracted leaves and measured the weight of it then decantation the solution. Evaporation of the solvent by heating without boiling the solution on a hot plate until a dense liquid dye obtained. Evaporating the solvent completely by putting dense dye in a vacuum oven at 45°C for 15 hour, the extracted pigment stored in the desiccator waiting to treat with polymer later.

The extraction of anthocyanin pigment from cherry: where the great amounts of anthocyanins, they are found in fruits and flowers. The concentration of anthocyanins in fruits is much higher than in vegetables[15].First washing the cherries with distilled water and remove the cores then mixing them with distilled water for the purpose of facilitating the process of extraction and juiced by using electric juicer-blender type VA-6770G/ HITACHI. The result juice contains a lot of fiber so it filtered with a polymer cloth (Berlun) then mixed with a bit of ethanol and followed by filtration using filter paper. Addition of ethanol to keep extracted pigment from rotting and to facilitate the filtration process. Evaporation of the solvent by heating on hot plate at 50°C and followed by vacuum oven at 45°C for 18 hour then stored it in order to be used later. The resulting cherry pigment has a sticky dense textures.

2.3. Apparatus

UV- Visible spectrophotometer is used, type UV-1800, (Shimadzu-Japan) with quartz cells (1 cm).

The Fourier transform infrared (FTIR) spectra were recorded on a FTIR 8400S-Perkin-Elmer spectrophotometer. The samples were pressed into tablets with KBr.

Hardness test is performed on the sample using Shore D with ASTM-D1415 standard at room temperature in order to analyze the effect of adding natural pigments on the PVC hardness.

Density test is performed using (Matsu Haku, China,

HIGH Precision DENSITY TESTER GP-120S with digital accuracy = $\pm$ 0.0001 g/cm^3).Which contain water at room temperature and the measure based on Archimedes low.

Thermal analysis were investigated by Netzsch (200 F3 Maia)differential scanning calorimeter (DSC), Germany according to ASTM D3418-03. Afforded T_g of the samples under a nitrogen gas. The heating rate was 10 °C/min over the temperature range 20–200 °C. The objective of this test is to determined T_g value in addition to the T_m value, if it's within the above ranges. Then the obtained T_g used in calculations depending on molecular models which its content the simplest idealized model of a linear molecule is the chain model without branching as show in fig. (3). For calculation the linear molecule is represented as a freely jointed chain, consisting of units (segments) of equal length[10].
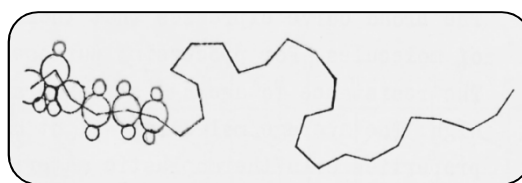

Fig. 3. *Model of a molecular chain[10].*

Considered as "bodyless". It is obvious that such a chain will continuously fluctuate. This model is used for statistical calculations. The chain diameter is in the order of 10^{-1} μm and the extended chain length can be 10^4 times larger.

The activation energy for chain rupture is about 60 kCal/mol (251 kJ mol^{-1}) so that at room temperature the value of the decisive factor in chain rupture as a thermal fluctuation process is about 101[10].

The resulting energy change from calculations was compared with bond energies listed in table 1.

3. Result and Discussion
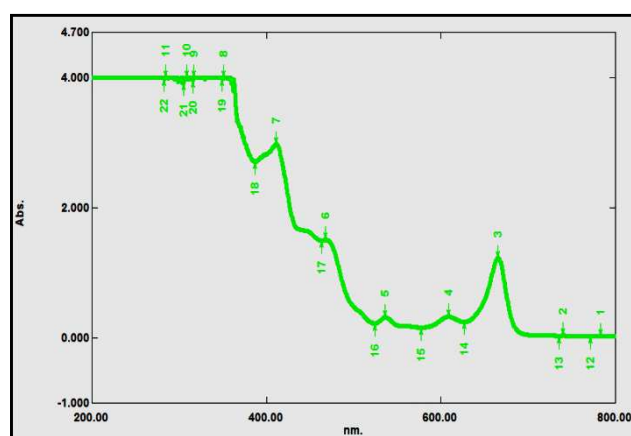
3.1. UV–Visible Spectroscopy Test

Fig. 4. *The absorption spectrum of alcoholic chlorophyll pigment.*

Fig. 4 and 5 show the absorption spectra of pure chlorophyll, and pure cherry anthocyanin in range 200-800

nm. Standard chlorophyll *a* and *b* absorb with narrow bands (maxima) in the blue (near 428 and 453 nm) and red (near 661 and 642 nm) spectral ranges[16]. Therefore the extracted citrus aurantium leaf chlorophyll is mainly chlorophyll *a* due to its absorb bands (near 411 nm) and (665.5 nm) spectral ranges close to chlorophyll *a*. Standard anthocyanin visible max. 515-545 nm and standard absorbance band of the cherry pink solution near 515 nm[14, 17]. The extracted cherry anthocyanin has absorption band at 535.5 nm.
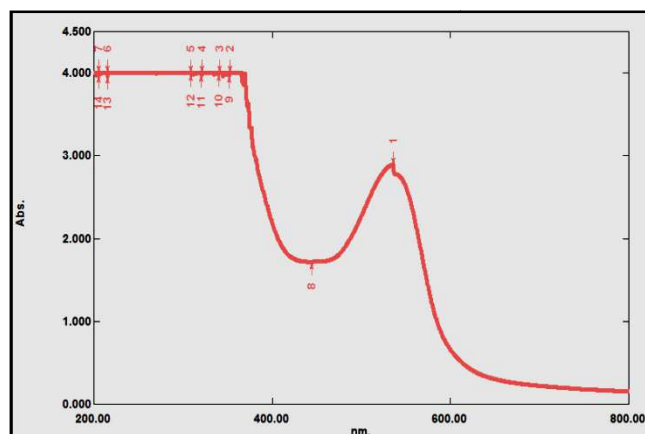

Fig. 5. *The absorption spectrum of aqueous cherry anthocyanin pigment.*

3.2. FTIR Analysis

Physicochemical characterization of pure pigment with KBr using infrared spectroscopy, fig. 6 and 7 represent the FTIR spectrums of pure chlorophyll, and pure cherry anthocyanin, respectively. It is clear from tables 2 and 3 that the transmission pattern of chlorophyll and anthocyanin spectrums is similar to their standards. Detailed examination of the spectrums show characteristic bands for both pigments.
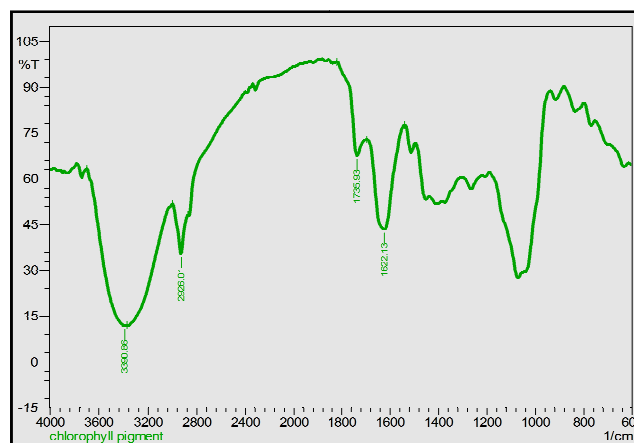

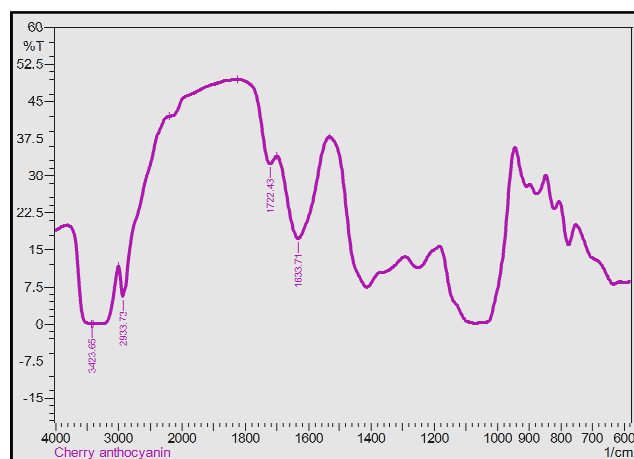
Fig. 6. *FTIR spectrum of extracted chlorophyll pigment.*

Fig. 7. *FTIR spectrum of extracted cherry anthocyanin pigment.*

Table 2. *Bonds wave number of chlorophyll pigment.*

Type of bond	Stander transmission peak[18]/cm^{-1}	Experimental transmission peak/cm^{-1}
C=O of aldehyde group	1618-1653	1622.13
C=O of ester group	1718-1740	1735.93
C─H	2916	2926.01
OH group	3362-3421	3390.86
Hydroxyl group	3750	3749

Table 3. *Bonds wave number of cherry anthocyanin pigment.*

Type of bond	Stander transmission peak[17]/cm^{-1}	Experimental transmission peak/cm^{-1}
C=C of benzene ring	1629.97	1633.71
carbonyl group	1724.92	1722.43
aliphatic hydrogen	2934.98	2933.73
OH group	3429	3423.65

Characterization of the Blended samples with KBr using infrared spectroscopy, fig.8 and 9 show FTIR spectrum of pure PVC, and with chlorophyll and anthocyanin pigments, respectively; in the range between 600 and 4000 cm^{-1}. Table4 contain bands wavenumber variation for pure PVC and with chlorophyll and anthocyanin pigments.

Pigments are strengthen band energy due to their denoting electron in 3% and 7% pigment. Other effect of pigments are shifting spectra to lower wavenumbers due to physical interaction between polymers and pigments.Generally, all these variation can be attributed to the interaction between the addition material and base one such interaction is physical interaction. So its effect mainly on the secondary bond not on the primary bond. Thus the FTIR spectrums show small effect on the absorption band, which indicate clearly no effect on the primary bond.
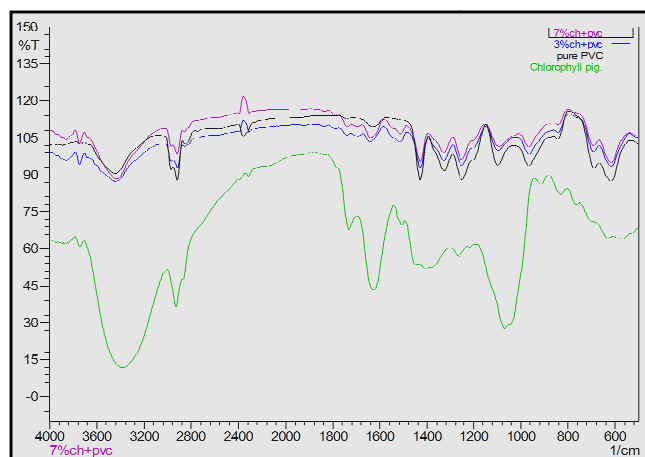
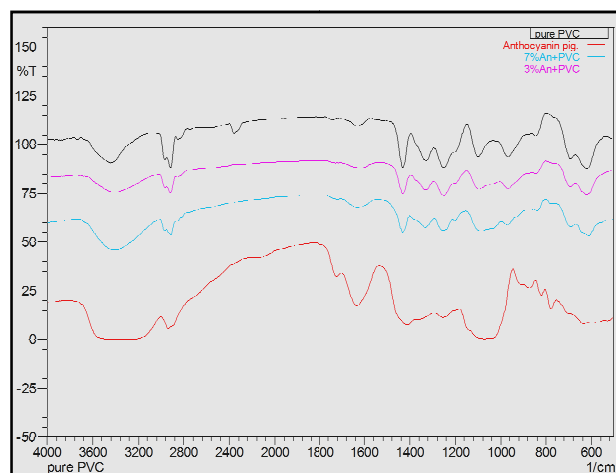**Fig. 8.** FTIR spectra of chlorophyll, PVC, 3%, 7% chlorophyll.

Fig. 9. FTIR spectra of anthocyanin, PVC, 3%, 7% anthocyanin.

Table 4. Bands wavenumber variation forPVC with pigments.

Type of bond	Stander PVC peak[19]/cm^{-1}	Exp. PVC peak/cm^{-1}	3% Ch. peak /cm^{-1}	7% Ch. peak/cm^{-1}	3% An. peak /cm^{-1}	7% An. peak/cm^{-1}
	2964	2970.38	2970.38	2970.38	2970.38	2970.38
CH and CH$_2$ stretching	2915	2912.51	2910.58	2912.51	2912.51	2912.51
	2853	2848.86	2848.86	2852.72	2848.86	2850.79
	1426	1429.25	1427.32	1429.25	1427.32	1425.4
CH$_2$ and CH deformation	1329	1328.95	1330.88	1330.88	1332.81	1332.81
	1253	1251.80	1253.73	1253.73	1255.66	1255.66
C-C stretching	1095	1097.5	1095.57	1093.64	1097.5	1080.14
CH$_2$deformation	964	964.41	964.41	964.41	966.34	966.34
C-Cl stretching	686	688.59	692.44	692.44	680.87	678.94
	607	613.36	613.36	613.36	609.51	611.43

3.3. Differential Scanning Calorimetry (DSC) Test

Fig. 10shows the DSC analysis of pure PVCwith pigments.

$$E_a = \Delta H^{\ddagger} + RT \qquad (1)[20, 21]$$

Where:

E_a: activation energy (kJ mol^{-1}).

$\Delta H^{\ddagger}$: activation enthalpy (kJ mol^{-1}).

RT: thermal energy (work) pd$'$v = RT (kJ mol^{-1})

According to molecular models (the activation energy for chain rupture is about 60 kCal/mol (251 kJ mol^{-1}) so that at room temperature the value of the decisive factor for chain rupture as a thermal fluctuation process is about 101[10](page 4) for one mole.

$$\therefore E_a = \Delta H^{\ddagger} + RT = RTD_f \qquad (2)$$

Where:

R : the gas constant (0.0083 kJ K^{-1} mol^{-1})

T: the absolute temperature (K)

D_f : decisive factor

$$E_{a_{at\ R.T}} = 251 \ \text{kJ mol}^{-1}$$

$$E_a = \Delta H^{\ddagger} + RT = 251$$

Since RT value is small at room temprature which is equal to 2.47 kJ mol^{-1} comparing with $\Delta H^{\ddagger}$:

$$\therefore \Delta H^{\ddagger} \gg RT \qquad \rightarrow \qquad E_a \cong \Delta H^{\ddagger} \qquad (3)$$

$$E_a = \Delta H^{\ddagger} = RTD_f \qquad (4)$$

$$E_a = 0.0083 \ \text{kJ K}^{-1} \text{mol}^{-1} * 298.15 \ \text{K} * D_f = 251 \ \text{kJ mol}^{-1}$$

$$D_f = 101.43$$

$$\text{Each unit of } D_f = \frac{251}{101.43} = 2.475 \ \text{kJ mol}^{-1}$$

-Poly (Vinyl Chloride) Powder (PVC)

T_g of pure PVC = 86.3 ℃

$$E_a = RTD_f$$

$$251 = 0.0083 * 337.25 * D_f \quad \rightarrow \quad D_f = 84.13$$

$$\Delta D_f = D_{f\ at\ R.T} - D_{f\ at\ 86.3℃}$$

$$= 101.43 - 84.13 = 17.3$$

Addition E_a from different temp. $_{(25\ \&86.3℃)}$

$$= \Delta D_f * \text{Each unit of } D_f = 17.3 * 2.475$$

$$= 42.8175 \ \text{kJ mol}^{-1} \qquad (5)$$

$$E_{a\ at\ (86.3℃)} = 251 - 42.8175 = 208.1825 \ \text{kJ mol}^{-1}$$

$$\Delta T = 86.3 - 25 = 61.3℃$$

$$1℃ \equiv \frac{\text{Addition } E_a}{\Delta T} \equiv \frac{42.8175}{61.3} \equiv 0.698 \ \text{kJ mol}^{-1} \qquad (6)$$

- By Addition 3% Chlorophyll to PVC

The temperature of chain rupture falls to 86.2°C due to addition 3% chlorophyll

$$\therefore T_g = 86.2 \ °C$$

$$E_a = RTD_f$$

$$251 = 0.0083 * 359.35 * D_f \quad \rightarrow \quad D_f = 84.15$$

$$\Delta T = 86.2 - 25 = 61.2°C$$

Addition E_a from different temp.$_{(25 \ \& 86.2°C+3\% \ Ch.)}$

$$= 61.2°C * 0.698 \ kJ \frac{mol^{-1}}{°C} = 42.7 \ kJ \ mol^{-1}$$

Given energy by addition pigment $= 42.817 - 42.717$ (7)

$$= 0.099 \ kJ \ mol^{-1} (this \ given \ by \ 3\% \ chlorophyll)$$

$$E_{a \ at \ (86.2°C)} = 208.1825 - 0.099 = 208.08 \ kJ \ mol^{-1}$$

- By Addition 7% Chlorophyll to PVC

The temperature of chain rupture falls to 86.9°C due to addition 7% chlorophyll

$$\therefore T_g = 86.9°C$$

Repeat the same procedure for $T_g = 86.2 \ °C$ but at($T_g = 86.9 \ °C$)and the result shows in table 5.

- By Addition 3% Anthocyanin to PVC

The temperature of chain rupture falls to 84.8°C due to addition 3% anthocyanin

$$\therefore T_g = 84.8°C$$

Repeat the same procedure for $T_g = 86.2 \ °C$ but at($T_g = 84.8 \ °C$)and the result shows in table 5.

- By Addition 7% Anthocyanin to PVC

The temperature of chain rupture falls to 84.3°C due to addition 7% anthocyanin

$$\therefore T_g = 84.3°C$$

Repeat the same procedure for $T_g = 86.2 \ °C$ but at($T_g = 84.3°C$)and the result shows in table 5.

Results are arranged in table 5. And compared with the value of secondary bond energy (table 1) to detected approximately the type of destroyed secondary bond by pigments in PVC,which is listed in table 6.
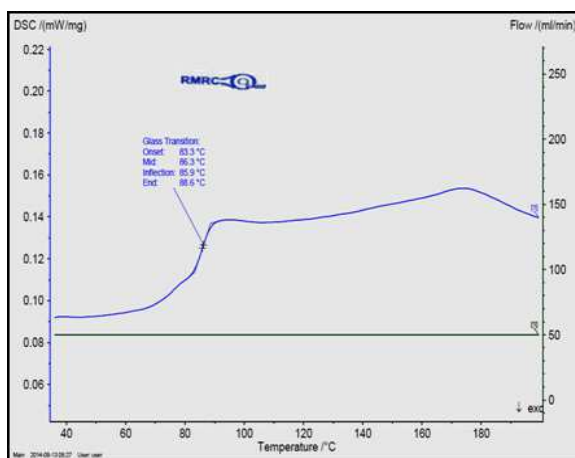
Table 5. Show the effect of natural pigment on PVC at R.T (25°C) & E_a (251 kJ mol^{-1}) with D_f (101.43).

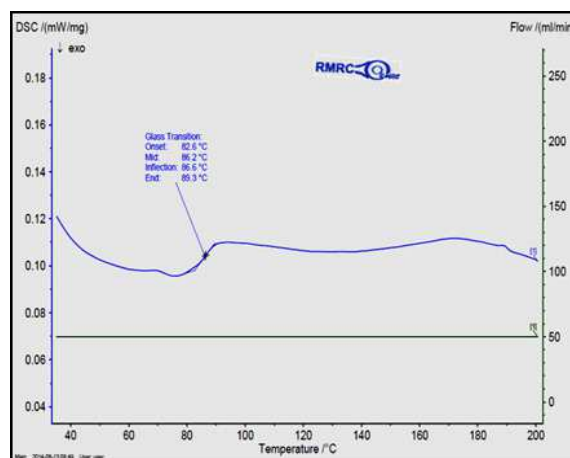| Substance	T_g (°C)	D_f	E_a at T_g (kJ mol^{-1})	AdditionE_a (kJ mol^{-1})
Pure PVC	86.3	84.13	208.18	42.8
3% chlorophyll	86.2	84.15	208.08	42.7
7% chlorophyll	86.9	84	208.57	43.2
3% anthocyanin	84.8	84.48	207.1	41.7
7% anthocyanin	84.3	84.6	206.75	41.4

Table 6. Expected destroyed secondary bond by pigments in PVC.

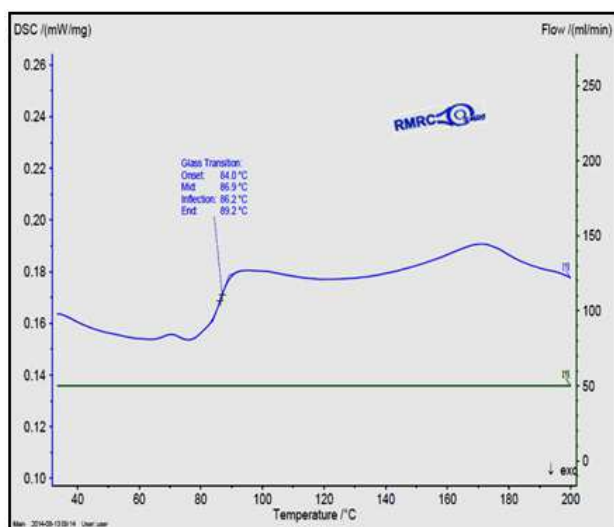| Substance	Given energy by addition pigment (kJ mol^{-1})	secondary bond energy[2] (kJ mol^{-1})	Expected type of bond present
3% chlorophyll	0.09		(Van der Waals bonds)
7% chlorophyll	0.38		*Dipole–induced dipole interactions
3% anthocyanin	1.1	< 2	Dispersion(London) forces.
7% anthocyanin	1.43	0.08 - 40	

*There is no dipole–induced dipole interactions because all PVC molecule have permanent dipole interactions.
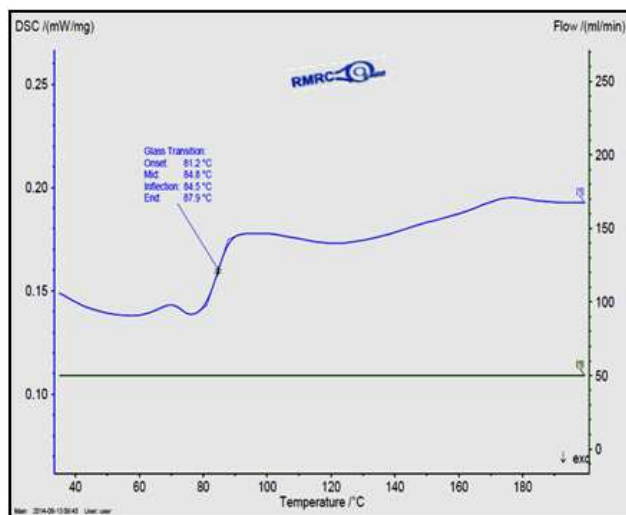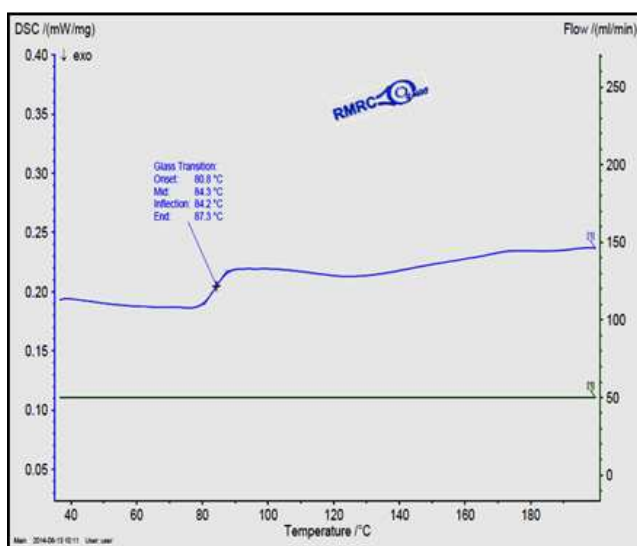

(a)

(b)

(c)

(d)

(e)

Fig. 10. *DSC analysis of (a) PVC with (b) 3% chlorophyll, (c) 7% chlorophyll, (d) 3% anthocyanin, and (e) 7% anthocyanin.*
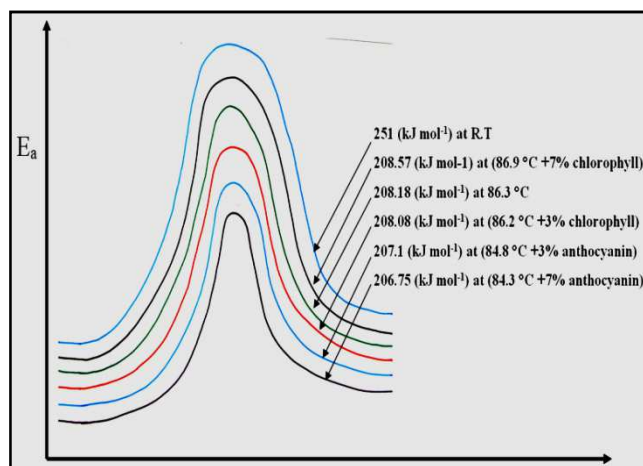

Fig. 11. *Activation energy for chain rupture in PVC.*

The results show that anthocyanin shows higher depression in glass transition temperature (T_g) of PVC than chlorophyll pigment, this due to many functional groups in anthocyanin. Fig. 11 shows activation energy for chain rupture in PVC at room temperature and changing of T_g that due to addition pigments.

Chlorophyll and anthocyanin well known as a plasticizer[22], thus it enhances breaking secondary bonds and making polymer molecule more free to move. Chlorophyll is a polar molecule with high molecular weight, and insoluble in water, so at lower concentration (3%) it break the secondary bond due to diffusion into PVC as its percent increase to (7%) less effect appear in PVC, this is due that chlorophyll absorbs energy [22,23].Anthocyanin has exchangeable proton, thus anthocyanin can exchange this proton with heavy metal and precipitated it. Anthocyanin is oily and water soluble compound with high polarity due to many hydroxyl group present, so it's easy to rupture secondary bonds during diffusion in the polymer result in lowering the glass transition temperature (T_g) by inter to the polymer structure easily. Although anthocyanin has larger effect than chlorophyll, but the effect of pigments on PVC are not great due to that hydrogen bonding in PVC is very weak.

3.4. Hardness Test

From fig.12, noticed first clear decreasing of hardness for PVC as chlorophyll percent increases, that is due to chlorophyll is plasticizer as provided, in a high percent of chlorophyll (> 0.2%) clear decreasing in mechanical properties. 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 50%) to get the same results [22].

3.5. Density Test

Fig.13shows the density behavior of pure and blends of PVC as increasing pigments percentage, the density decreasing due to the presence of pigments between the

polymer chains leaving vacancies.

Anthocyanin effect on PVC density by create voids between molecules then destroyed secondary bonds result in decreasing density. While chlorophyll hasn't the ability of completely destroyed of secondary bonds, so its slightly effect on PVC density.
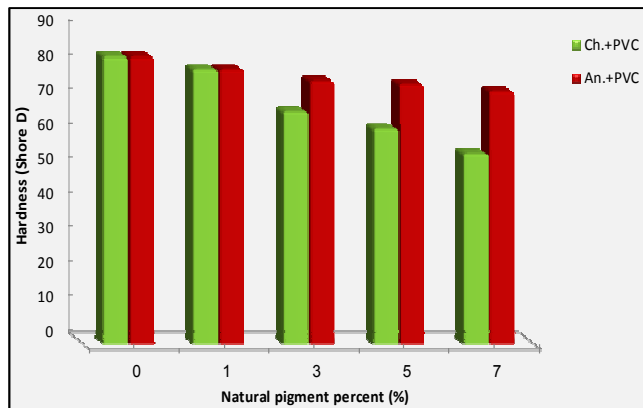

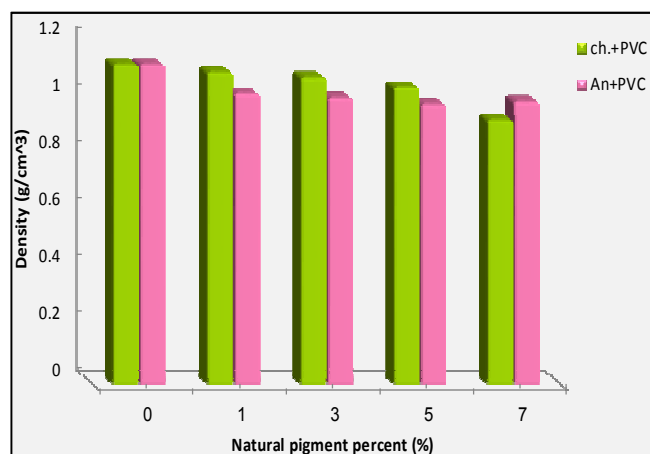**Fig. 12.** *Effect of pigments on PVC hardness.*

Fig. 13. *Effect of pigments on PVC density.*

4. Conclusion

From this work we can summarize the following conclusions:

1. Extraction procedure of natural pigments which done in similar ideas as in literature which confirmed by UV-Visible and FTIR spectrums.
2. FTIR spectrum of polymers with pigment show lightly effect on the absorption band, which indicate that there is no effect on the primary bond. There is just effect on secondary bond by physical interaction.
3. The DSC test showed that the percentage 3% chlorophyll gives maximum effect on PVC. And 7% anthocyanin has the highest effect.
4. The main attack of the pigments are to overcome the dispersion (London) forces in PVC polymer.
5. As chlorophyll concentration increase lead to decrease PVC hardness and density. As well as anthocyanin behavior.

6. The hydrogen bond in PVC is very week.
7. Finally, from all above result we conclude that the anthocyanin and chlorophyll pigment act as natural plasticizers by destroying the secondary bonds in these polymers which facilitate processability.

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