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Effect of carotene pigment on biopolymers

Jaleel Kareem Ahmed[1], Faten Chouman[2], Rusul M Abd Alradha[3]
[1, 3] Department of Polymer, Materials Engineering College, University of Babylon, Babylon, Iraq
[2] College of Pharmacy, Alsham Private University, Latakia, Syria

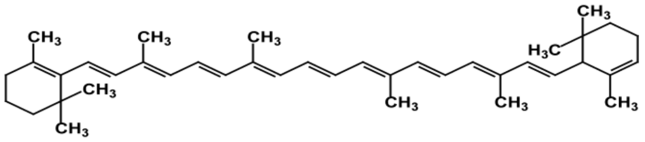
Abstract

Carotene pigment extracted from carrot by simple process. The pigment added by 3 and 7% to different biopolymers [poly(vinyl alcohol) (PVA), poly(methyl methacrylate) (PMMA), cellulose and starch]. Different tests are carried out such as differential scanning calorimeter (DSC), ultra-visible spectra and hardness. Ultra-visible spectra confirmed that there are physical interactions between carotene and biopolymers, thus the effects of the pigment are on the secondary bonds (engineering bonds) and not on the primary bonds. Also results show that carotene increases the hardness of the study polymers, thus it increase the glass transition temperature (T_g) of the PVA, PMMA and starch while lowering the T_g of cellulose, this is due to the high molecular weight of cellulose comparing with starch. The increasing of T_g of the biopolymers means carotene support the strength of the secondary bonds in these polymers by the delocalized π-electrons (carotene molecule has π-bonds can share it to the polymer to support their strength).

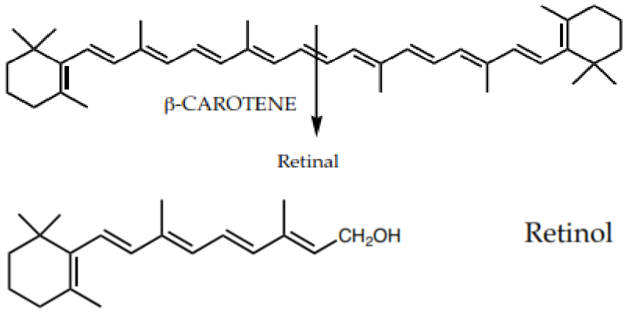
Keywords: carotene pigment, PVA, PMMA, cellulose, starch, glass transition temperature (T_g)

Introduction

Carotene is a naturally occurring substance in carrot as β-carotene with molecular weight of (536 g/mol) and chemical formula of ($C_{40}H_{56}$) [1]. Carotene possesses eleven conjugated double bonds in its chemical structure capable of absorbing visible and UV light with high efficiency which can be dissipated as harmless heat. Thus, carotene protects the eye from incident UV light [2, 3]. Carotene is a hydrocarbon substance that is lipophilic and water insoluble, does not have active functional groups. Therefore, it is chemically stable [4].



Carotene split by an enzymatic effect in the liver and the accurate intestine into two molecules from vitamin **A** (Retina) [1].



In 2007, Zuhair Alassady [5] had studied the effect of natural dyes such as chlorophyll, β-carotene, and anthocyanin as coloring, retarders and plasticizer to commonly used polymers such as polyvinyl chloride (PVC), epoxy resins and unsaturated polyesters by formulating different types of samples with different weight percentages of dyes. The aim of this research is to investigate the behavior of concentrated carotene dye in carrot and its effects on the physical role of naturally occurring biopolymers that exist in human body by measuring the temperature of glass transition of the polymers and estimating the associated energy.

The studied polymers are PVA, which is a white odorless substance that dissolves in warm water. It is used in pharmaceutical industry to make eye drops like artificial tears and contact lenses solution.

PMMA that has a molecular formula of ($C_5O_2H_8$)n is a white water insoluble biopolymer that allows the light to pass through with more than 95%. Thus, it is used as bone cement in fixation of artificial joints where it fills the spaces between the joint and the surface of the bone. PMMA is also used in the industry of artificial dental crown and fillings [6].

Cellulose $(C_6H_{10}O_5)_x$ is a polysaccharide biopolymer that is white in color. It does not have a metabolic pathway in human body and its role is dynamic only (to discharge waste). Cellulose is the main constituent of the plant cell wall. It is like starch a complex carbohydrate. Cellulose is not soluble in water and not permeable through plant cell membrane. Cellulose does not exist as naturally pure substance. Cotton fibers represent the purest state of cellulose. Cellulose is used in manufacturing of synthetic silk and water sweetening membranes [7].

Starch $(C_6H_{10}O_6)_n$ is a naturally occurring polysaccharide that exist as white fine powder that is slightly soluble in water and it has less molecular weight than cellulose. Starch is metabolized and stored in human body and animals as collagen. It has many uses in nutrition, fabrics and pharmaceutical industries [7].

Results

In this research carotene, yellow natural pigment, unsaturated hydrocarbon, it presents in 3 chemical form i.e.

α, β, γ. β form mainly exists in carrot. 22 π delocalized electrons on the molecule body. Thus carotene molecule is a good antioxidant and good π- electron donator. In the middle of the molecule (the weakest molecule link) carotene splits in liner to two molecules of vitamin A. For the above specification, the research selects carotene for more investigation on glass transition temperature (T_g) which is a function of secondary bonds (engineering bonds) in polymers as well as to study its effects on the T_g as a function of concentration.

Poly(vinyl alcohol) PVA biopolymer- carrot:
The results are listed in the table 1

Table 1

Polymer	Glass transition temperature (T_g) ℃	Melting temperature (T_m) ℃
poly(vinyl alcohol) PVA	78.69	187.89
3% carrot	90.24	186.32
7% carrot	92.31	186.04

It seems that carrot highly supports the secondary bonds i.e. hydrogen bond by donating π-electrons to strength the secondary bonds, thus the T_g rises from 78.69 to 90.24 ℃ upon addition of 3% carrot as the concentration increases to 7% carrot, T_g still increases. This result reflect on all alcohols and it can say carrot push alcohol polymer to more rigid polymer (more solid) while reduce the freedom of alcohol molecule e.g. ethanol which means reduce its biological effect on human body.
From the glass transition temperature (T_g) data it is possible to calculate energy transfer between polymer and addition carrot. According to polymer molecular models, the activation energy for polymer chain rupture (ending of friendly relations, or breaking apart) is about 251KJ mol^{-1}at room temperature, so that the value of decisive factor for chain rupture as a thermal fluctuation process is about 101 for one mole.

$Ea=\Delta H^{\ddagger}+RT= 251\ kJ\ mol^{-1}$

$\Delta H^{\ddagger} \gg RT$

$\therefore\quad Ea=\Delta H^{\ddagger}=RTD_f$

Where:
Ea: activation energy for polymer chain rupture (kJ mol^{-1})

$\Delta H^{\ddagger}$: Activation enthalpy for polymer chain rupture (kJ mol^{-1})

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

T: the absolute temperature (K)

D_f: decisive factor

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

$D_f=101.43$

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

a) Thus T_g for pure PVA=78.69 ℃

$Ea=RTD_f$

$251=0.0083*351.84*D_f$

$D_f=85.958$

$\Delta D_f=D_{f\text{ at R.T}}-D_{f\text{ at }78.69\ ℃}=101.43-85.958$

$\Delta D_f =15.472$

Addition $Ea_{\text{from }(25\ \&\ 78.69\ ℃)}=\Delta D_f$ *Each unit of D_f

$Ea_{\text{from }(25\ \&\ 78.69\ ℃)}=15.472*2.475=38.293\ kJ\ mol^{-1}$

$Ea_{\text{at }(78.69\ ℃)}=251-38.293 =212.707\ kJ\ mol^{-1}$

$\Delta T=78.69 -25=53.69℃$

$1℃ \equiv Ea_{\text{at }(25\ \&\ 78.69\ ℃)} /\Delta T$

$1℃\equiv 38.293 / 53.69 \equiv 0.71\ kJ\ mol^{-1}$

b) Addition 3% carrot

$T_g=90.24℃$

$Ea=RTD_f$

$251=0.0083*363.39*D_f$

$D_f=83.22$

$\Delta T=90.24-25=65.24℃$

Addition $Ea_{\text{from }(25\ \&90.24℃+3\%\text{ carotene})}= 65.24℃*0.71\ kJ\ mol^{-1}$

$Ea_{\text{from }(25\ \&90.24℃+3\%\text{ carotene})}=46.320\ kJ\ mol^{-1}$

Given energy from addition 3% carrot = 38.293 -46.320

Given energy $_{(\text{from addition 3\% carrot})}$ = -8.027 kJ mol^{-1}

$\therefore Ea_{\text{at }(90.24℃)}=212.707 -(-8.027)= 220.734\ kJ\ mol^{-1}$

From temperature difference = 90.24-78.69 = 11.55℃

Given energy by addition 3% carrot = 11.55* 0.71

Given energy $_{(\text{from addition 3\% carrot})}$ = -8.2 kJ mol^{-1}

$\therefore Ea_{\text{at }(90.24℃)}=212+8.2 = 220.2\ kJ\ mol^{-1}$

c) Addition 7% carrot

$T_g=92.31℃$

$Ea=RTD_f$

$251=0.0083*365.46*D_f$

$D_f=82.756$

$\Delta D_f =101.43-82.756= 18.674$

From temperature difference = 92.31-25 = 67.31℃

Given energy from (25 &92.31℃+7% carrot)= 67.31℃*0.71 kJ mol^{-1}

Given energy $_{(\text{from 25 \&92.31℃+7\% carrot})}$=47.790 kJ mol^{-1}

Given energy from addition 7% carrot = 38.293 -47.790

Given energy $_{(\text{from addition 7\% carrot})}$ = -9.497 kJ mol^{-1}

$\therefore Ea_{\text{at }(92.31℃)}=212.707 -(-9.497)= 222.204\ kJ\ mol^{-1}$

The results are tableted in tables 2 and 3 and fig (1c).

Table 2: Shows the effect of carotene on PVA at R.T (25°C) & Ea (251 kJ mol^{-1}) with D_f (101.43).

Substance	Tg (°C)	Df	Ea at Tg (kJ mol^{-1})	Given Ea from heating and addition carotene (kJ mol^{-1})
Pure PVA	78.69	85.958	212.707	38.293
3% carotene	90.24	83.22	220.734	46.320
7% carotene	92.31	82.756	222.204	47.790

Table 3: Shows the given energy by addition carotene to PVA.

Substance	Given energy from addition carotene (kJ mol^{-1})
3% carotene	-8.027
7% carotene	-9.497

Poly(methyl methacrylate) PMMA- carrot system

Table 4: The T_g data are listed in table

Polymer	Glass transition temperature (T_g) °C	Melting temperature (T_m) °C
poly(methyl methacrylate) PMMA	98.54	244.57
3% carrot	106.02	251.94
7% carrot	107.66	265.3

Poly(methyl methacrylate) PMMA is industrial biopolymer with polar group. It belong to thermo-elastic plastics, the definition is basically the same as with elastomers, but instead of a chemical cross-linking there is a physical cross-linking and a glass transition temperature above 0 °C, thus physical cross-linking is electronic interaction which is strengthen by electron donor molecule carotene result in rises in T_g which is agree with the research results as shown in table (4). Thus carrot improve the hardness more heat resistances and insolubility of PMMA which is more suitable for PMMA in teeth and bones uses.

Calculations carried on as in previous system PVA-carrot. The result listed in tables 5, 6 and figure (1d).

Table 5: Shows the effect of carotene on PMMA at R.T (25°C) & Ea (251 kJ mol^{-1}) with D_f (101.43).

Substance	Tg (°C)	Df	Ea at Tg (kJ mol^{-1})	Given Ea from heating and addition carotene (kJ mol^{-1})
Pure PMMA	98.54	81.361	201.33	49.670
3% carotene	106.02	79.758	205.943	54.283
7% carotene	107.66	79.430	207.042	55.382

Table 6: Shows the given energy by addition carotene to PMMA.

Substance	Given energy from addition carotene (kJ mol^{-1})
3% carotene	-4.613
7% carotene	-5.712

Cellulose- carrot

Cellulose is a natural-biopolymer with high molecular weight comparing with starch. It is insoluble in most of solvents and acts as solid waste removal in human body. The T_g data are shown in table (7).

Table 7

Polymer	Glass transition temperature (T_g) °C	Melting temperature (T_m) °C
Cellulose	88.78	339.93 d
3% carrot	78.50	333 d
7% carrot	77.97	339.82 d

Cellulose differs from the three biopolymers (PVA, PMMA and starch) due to its T_g reduction upon addition of carrot. This reflect the unique structure of cellulose which characterize by high density of covalent and hydrogen bonds which make the structure highly compact and cohesive push cellulose to be insoluble and undigested. Thus carrot enter this structure by diffusion process breaking secondary bonds to reduce its T_g value. Table (7) shows that the most effect carrot percent is 3% while 7% shows no more reduction in T_g.

Calculation shows the energy transfers during addition carrot see tables 8, 9 and figure (1b).

Table 8: Shows the effect of carotene on cellulose at R.T (25°C) & Ea (251 kJ mol^{-1}) with D_f (101.43).

Substance	Tg (°C)	Df	Ea at Tg (kJ mol^{-1})	Given Ea from heating and addition carotene (kJ mol^{-1})
Pure cellulose	88.78	83.55	206.747	44.253
3% carotene	78.50	86.017	199.409	36.915
7% carotene	77.97	86.135	199.043	36.549

Table 9: Shows the given energy by addition carotene to cellulose.

Substance	Given energy from addition carotene (kJ mol^{-1})
3% carotene	7.338
7% carotene	7.704

Starch- carrot

Starch is a bio-natural polymer which is slightly water soluble and can be digested in human body comparing with cellulose. Its T_g is shown in table (10).

Table 10

Polymer	Glass transition temperature (T_g) °C	Melting temperature (T_m) °C
Starch	55.33	265.31/279.87 d
3% carrot	64.7	264.02/277.45 d
7% carrot	62.53	262.98/279.09 d

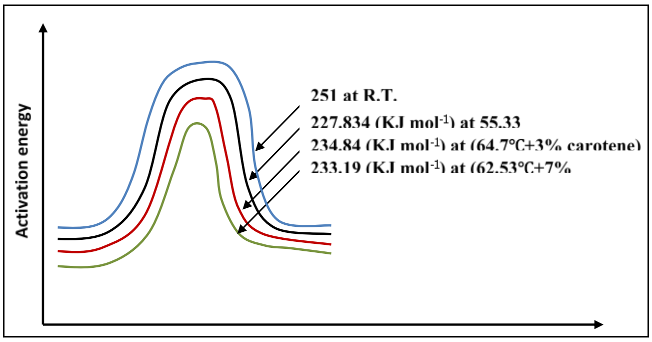
Calculation shows the energy transfers during addition carrot see tables 11, 12 and figure (1a).

Table 11: Shows the effect of carotene on starch at R.T (25°C) & Ea (251 kJ mol^{-1}) with D_f (101.43).

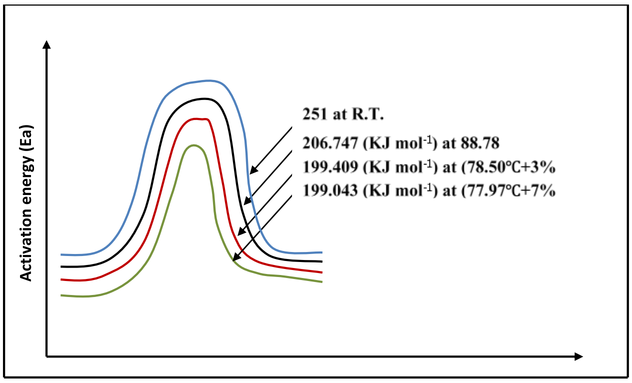
Substance	Tg (°C)	Df	Ea at Tg (kJ mol^{-1})	Given Ea from heating and addition carotene (kJ mol^{-1})
Pure starch	55.33	92.07	227.834	23.166
3% carotene	64.7	89.51	234.84	30.172
7% carotene	62.53	90.09	233.19	28.522

Table 12: Shows the given energy by addition carotene to starch.

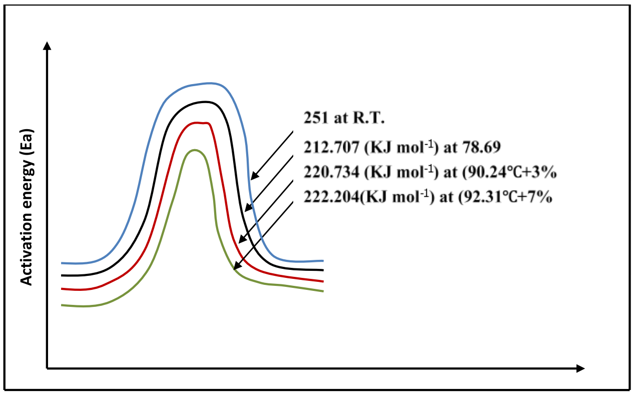
Substance	Given energy from addition carotene (kJ mol^{-1})
3% carotene	-7.006
7% carotene	-5.356



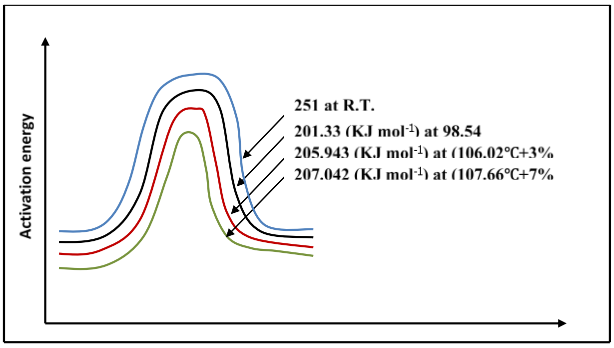
(a)



(b)



(c)



(d)

Fig 1: Activation energy for chain rupture in (a) starch, (b) cellulose, (c) PVA and (d) PMMA as a function of carotene percent.

Discussion

Carotene in carrot is mainly β-carotene.
Carotene is a good π-electron donor.
Carotene good missible with biopolymers like PVA, PMMa, cellulose and starch.
Carotene enhances cellulose in the direction of solubility and digestion.
Carotene reduces the ability of starch storage in human body.
Carotene reduces the activity of alcohol in human body.
Carotene improves the uses of PMMA in tooth and bone industry.
Carotene is a good visible-ultraviolet light absorber and disappiated as a non-harmful heat.
Carotene effects on glass transition temperature (T_g) of biopolymers are not a function of its concentration.
Carotene is a bio-natural yellow pigment is insoluble in most solvents.

Methods

Materials used

Polyvinyl alcohol (PVA), poly methyl methacrylate (PMMA), cellulose and starch were investigated in this study.

Polyvinyl alcohol (PVA)

PVA with M.W. = (125000), melting point= (165.19 ºC) and polymer degree (1700-1800), molecular formula $(C_2H_4O)_n$ from India company TITAN BIOTECH LTD.

Poly (methyl methacrylate) powder (PMMA)

Poly (methyl methacrylate) from Shnghai Dental Materials Co., Ltd.

Cellulose Powder

Cellulose $(C_6H_{10}O_5)_n$ from India company TITAN BIOTECH LTD.

Starch Soluble

Soluble starch $(C_6H_{10}O_5)_n$ melting point = (162.20 ºC) from India company TITAN BIOTECH LTD.

Preparation of samples

Fresh carrot juice was prepared by mechanical blending in a blender. The juice was then centrifuged in a centrifuge SCILOGEX, LLC manufactured by American with 3500 pph/min. After that, the product was dissolved in chloroform (to reform β-carotene crystals) then the mixture was placed in Vortex Mixter manufactured by Velop Scientifica. Then, the mixture is heated to 50 ºC in an oven to melt completely and filtered thereafter. Pure β-carotene is obtained by evaporation of the final filterate. The conducted physical measures included density, melting point and absorbance. Samples were prepared from these four polymers with pure β-carotene in two concentrations 3% and 7% as follows:

0.97g polymer + 0.03g β-carotene to obtain 3% concentration
0.93g polymer + 0.07g β-carotene to obtain 7% concentration

The samples were prepared by placing the different mixtures in a glass container for an hour then diethyl ether $(C_2H_5)_2O$ (molecular weight=(74.12), boiling point (35-36 ºC) obtained from (Eurolab – UK)) is added to the samples and manually stirred thoroughly. The mixture is then left to evaporate the solvent at lab temperature. The final sample powder is stored in glass containers to measure the values of Tg.

Competing interests

The authors declare no competing interests.

Author Contribution statement

J.K. Ahmad performed the activation energy calculations and wrote the conclusions. (50% of the article).

F. Chouman designed and performed the Experimental work and analyzed the samples. (40% of the article).

R. M. Abd Alradha wrote the body of the article (The introduction, material and methods, the results, and the references) (10% of the article).

References

1. Rettie Vitamin A. medical chemistry 562P-vitamins (and minerals).
2. Kevin Davies. Plant Pigment and their Manipulation, Annual Plant Reviews, Blackwell Publishing Ltd, UK, 2004, 14.
3. Castenmiller JJ, West CE. Bio-availability and bioconversion of carotenoids. Ann. Rev. Nutr. 1998; 18:19-38.
4. Parker RS, *et al*. Bio-availability of carotenoids in human subjects. Proc. Nutr. Soc. 1999; 58:1-8.
5. Al-Asadee. Addition of Some Natural Pigments As Colorants And Stabilizers Materials For Polymers, PH. D. thesis, Engineering college, Babylon University, 2007.
6. Ravve A. Principles of Polymer Chemistry, 3rd edition, Springer Science + Business Media, LLC, USA, 2012, 17.
7. Fred W, Billmeyer JR. 'Text Book of Polymer Science', John Wiley, 1984.