Molecular Interactions of Poly (methylmethacrylate), Poly (vinyl alcohol), Poly(ethylene glycol), Chitosan, Cellulose and Starch Polymers with Iodine

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Abstract

The interactions betweenpoly(methylmethacrylate)(PMMA),poly(vinylalcohol) (PVA) poly(ethylene glycol)(PEG)as industrial biopolymers andchitosan, cellulose, starch as natural biopolymers with iodine(I_2) were investigated using diethyl ether as a solvent. 5% of I_2 was added to each polymer and soaked in the solvent. The interactions were investigated using concepts of the activation energy(Ea), Decisivefactor (Df) and the changing in the glass transition temperature (ΔTg's). Therefore, the differential scanning calorimeter (DSC) was used to monitorthe thermal transitions. The optical microscope(OM) device was used to study the surface morphologies.Resultsshowed a clear depression in the glass transition temperatures (T_g's) for all polymers(as well as new colors appear) except cellulose still unaffected .It appears that cellulose molecules coated with a film prevent iodine to diffuse through the network structure of cellulose thus no effected its color or its Tg which indicates that molecular structure of cellulose quite different from that of starch and for this fact cellulose not soluble by a solvent and undigested in the human body. The depression inTg values of polymers indicate that iodine ruptures the engineering bonds of the polymers. The most effected Tg is of chitosan (lowered by 40.23˚C, this mean that iodine ruptures both hydrogen bonding through nitrogen and oxygen atoms in chitosan molecule.

From T_g values, it seems that iodine can acts as moderate plasticizer, by diffusing through the net of synthetic and natural biopolymers ruptures their secondary bonds result in depression of their T_g except in case of cellulose.

The order of T_g depression is:

Chitosan (40.23)>PMMA (27.89)>starch (22.29)>PVA (13.89) >PEG (5.78)>cellulose (0)

Which showed no distinguish between natural and synthetic biopolymers.

From T_g values calculation of the energy given by the addition of iodine to the polymers was done and shown the following order:

chitosan(27.394)>PMMA(18.442) =starch(18.414)>PVA(9.316)>PEG(4.315)>cellulose(0)

Keywords: *MolecularInteractions, Activation Energy, Decisive Factor, Secondary Forces, GlassTransition Temperature, Dipole Moment.*

Introduction

In the polymer, there are two types of interactions, primary bonds in its backbone and secondary forces among their chains. Primarybonds includes ionic,covalent, coordinate and metallicbond.Secondaryforces are generally known as physical bonds, secondary valence, intermolecular forces, or van der Waals force.Three types of secondary bonds are recognized:dipole forces, induction forces and dispersion [1,2]

Secondary or physical bonds are weak in comparison to the primary or chemical ones and exist between virtually all atoms or molecules, but its presence may be obscured if any of the three primary bonding types is present. Secondary forces are evidenced for the inert gases, which have stable electron structures, and, in addition, between molecules in molecular structures that are covalently bonded [2] The energy of the intermolecular attractive forces varies as the inverse sixth power of the intermolecular distance ($P.E = 1 / r^6$). As with primary-bonds, repulsion arises when the atoms approach more closely than an equilibrium distance of 3-5 Å.The energy of typical secondary forces is8-40 kJ mol^{-1}, divided among its three types according to the polarizability and dipole moment of the bonding molecules [1] The physical properties of polymer molecules are influenced not only by their composition, but also by their size and by the nature of their primary and secondary forces. Secondaryforces are not of great importance in the formation of stable chemical compounds. They lead, rather, to the aggregation of separate molecules into solid and liquid phases. As a result, many physical properties such as volatility, viscosity, surface tension, frictional properties, miscibility, and solubility are determined largely by intermolecular forces. Due to the large sizes of polymeric molecules, the secondary forces assume much greater roles in influencing physical properties than they do in small organic molecules. The cohesive energy is the total energy necessary to remove a molecule from a liquid or solid to a position far from its neighbors [1,3]

The activation energy (Ea) can be defined as a minimum energy which required for starting the chemical reaction [4].

Bond rupture can be explained when stress is applied any one of three principle reactions becomes possible. The three reaction mechanisms are radical, ionic, and ion-radical. The path depends on polymer composition, its physical state, and the medium in which the mechanochemistry is done. The influence of temperature on mechanochemistry is fundamental, how-even, and not always direct. The effects can be mainly indirect involving a change in (1) the physical state of the polymer, (2) the properties (viz. elasticity and viscosity), and (3) the mechanism of bond rupture. At lower temperatures, thermal motions are reduced, the relaxation processes are slower, and chain disentangling processes are longer. As a result of these features, the extent and reaction rate for mechanochemistry are generally higher at lower temperature [5].

Plasticizers are large organic molecular of low volatility that are added to plastics 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 .Plasticizers are particularly used for polymers that are in a glassy state at room temperature. These rigid polymers become flexible by strong interactions between plasticizers molecules and chain units, which lower their brittle-tough transition or brittleness temperature (T_b) (the temperature at which a sample breaks when struck) and their Tg value, and extend the temperature range for their rubbery or viscoelastic [6] state behavior

Thefollowingprocedure was used to determine the energy arises from bond rupture:

$Ea = \Delta H^{\ddagger} + RT$ .... (1)

The activation energy (Ea) is the summation of the activation enthalpy ($\Delta H^{\ddagger}$) and the work or the thermal energy (RT), as shown in equation (1).

According to polymer molecular models (the activation energy for chain rupture is about 60 kCal/mol (251 kJ mol^{-1}) at room temperature, so that the value of the decisive factor (D_f) for chain rupture as a thermal fluctuation process is about 101for one mole [7].

□ $Ea = \Delta H^{\ddagger} + RT = RTD_f$ .... (2)

Where:

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

T: the absolute temperature (K)

$Ea_{at\ R.T} = 251$ kJ mol^{-1}

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

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

$\square\Delta H^{\ddagger}\square RT \rightarrow Ea\square \Delta H^{\ddagger}$…………..................................... (3)

$Ea = \Delta H^{\ddagger} = RTD_f$……………………………….. (4)

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

$D_f = 101.43$

The energy of each unit of $D_f = 251/101.43 = 2.475\ kJ\ mol^{-1}$ …….………………… (5)

Experimental Work:

Materials used:

In this study, 5w% Iodine (I_2) was added to six polymers, three of them are synthetic typepoly (methyl methacrylate); PMMA, poly (vinyl alcohol); PVA and poly (ethylene glycol); PEG, and the other three are naturaltype chitosan, cellulose andstarchDiethyl ether used as a solvent.

The first three polymers supplied from Yonghui chemical Holdings Limited Company, china, while chitosan supplied from Shanghai Soyoung Biotech. Inc. China.Corn starch which is a white powder, was obtained from local markets. Iodine was purchased from Flucku, a Swiss company.

2. Preparation of samples:

Iodine (5wt %) was added and mixed with the following polymers: PMMA, PVA, PEG, chitosan, cellulose andstarch.This mixture was soaked with 30 ml of diethyl ether until evaporated it at room temperature. The resultant solid product was grinded by an electric grinder to obtain a powder form. The powder was examined by differential scanning calorimeter (DSC) to determine the glass transition temperature (T_g). Optical Microscope (OM) was used to studythe surface morphology.

Results and Discussion

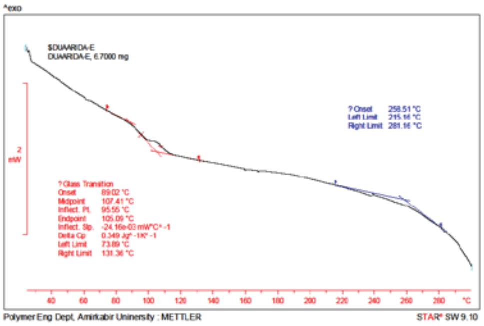


Fig (1): DSC curve of PMMA

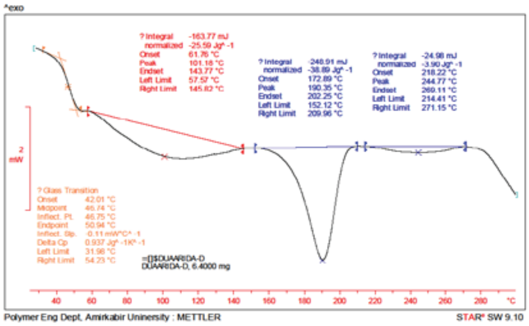
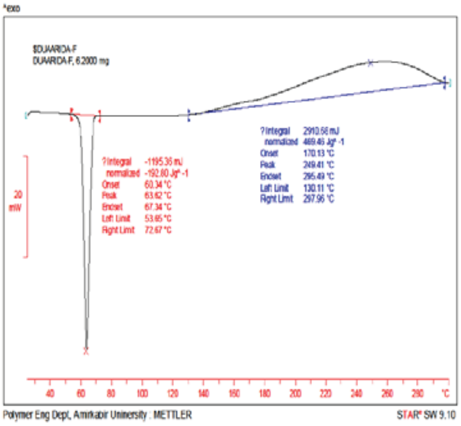


Fig (2): DSC curve of PVA



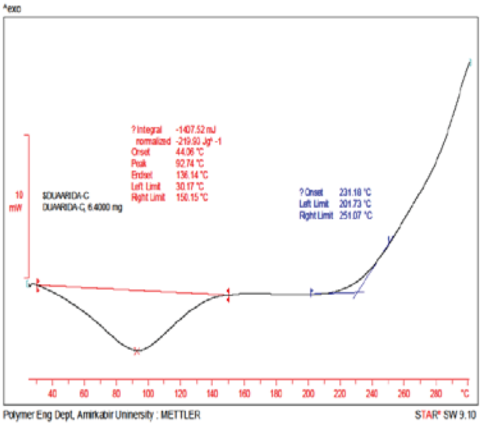


Fig (3): DSC curve of PEG

Fig (4): DSC curve of chitosan

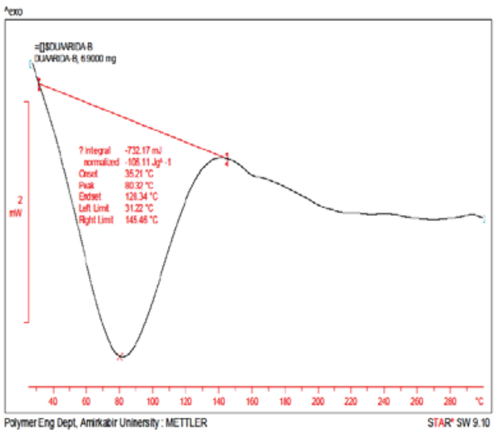


Fig (5): DSC curve of cellulose

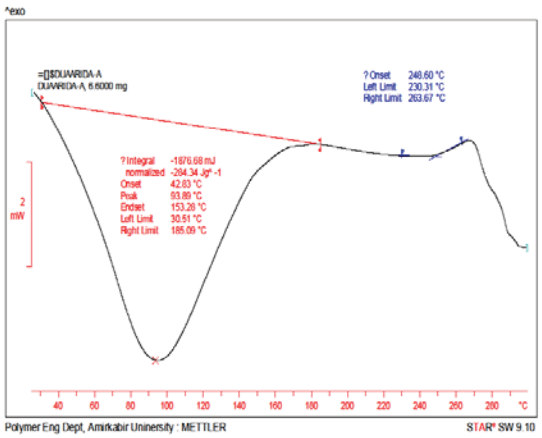


Fig (6): DSC curve of starch

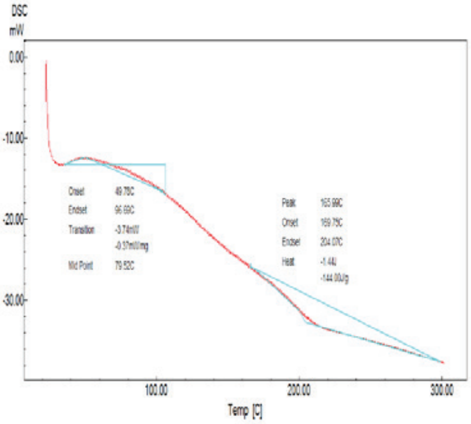


Fig (7): DSC curve of(PMMA /5wt%I$_2$) composite

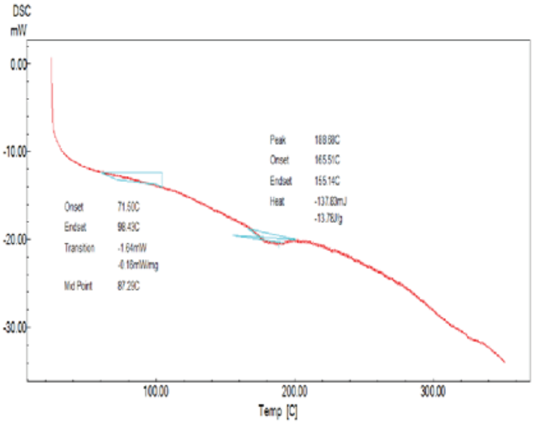


Fig (8): DSC curve of(PVA/5wt% I$_2$) composite

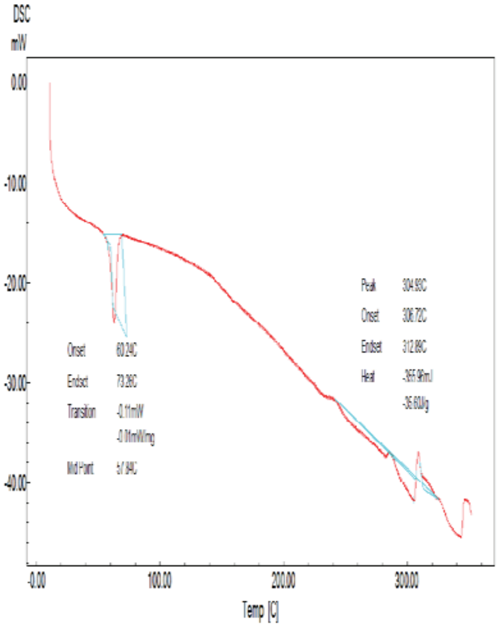


Fig (9): DSC curve of(PEG /5wt%I$_2$) composite.

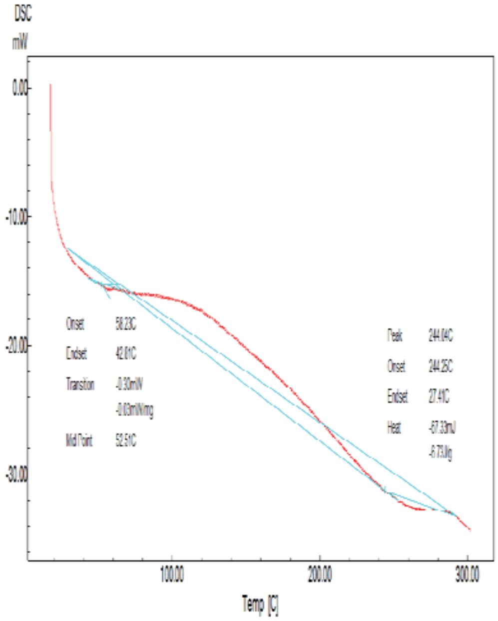
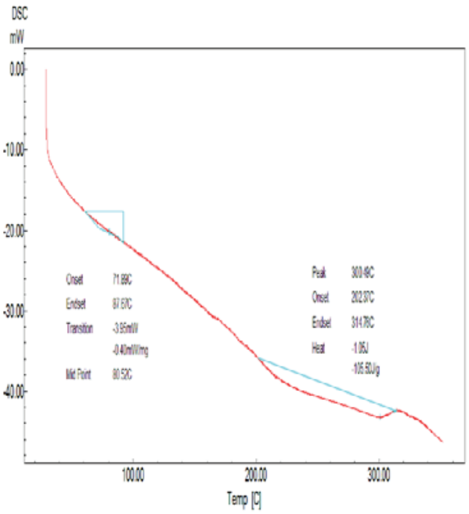


Fig (10): DSC curve of (chitosan/5wt%I$_2$) composite



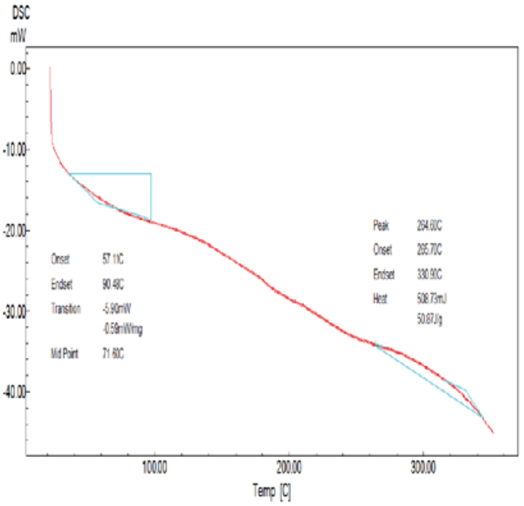


Fig (11): DSC curve of(cellulose/5wt%I_2) composite, Fig (12): DSC curve of(starch/5wt%I_2) composite.

These figures utilized to determining the glass transition temperatures (Tg) for pure polymers and their composites with 5(wt. %) I_2. Equations 1-5 (in the theoretical part) were used to calculate Ea and Df,as shown in table 1.Sample of calculations is done for pure PMMA andPMMA/5(wt. %) I_2 as follow:

For pure poly (methyl methacrylate) (PMMA):

T_g of pure PMMA=107.41□ (From fig.1)

Since Ea=R*T*$D_f$that means:

251=0.0083□380.56□D_f

D_f=79.46

$\Delta D_f = D_{fat\ R.T} - D_{fat107.41□}$

ΔD_f =101.43−79.46= 21.97

Addition $Ea_{from\ (25\ to107.41□)}$ =ΔD_f□Each unit of D_f

$Ea_{from\ (25\ to107.41□)}$ =21.97□2.475=54.37 kJ mol^{-1}............................... (6)

$Ea_{at\ (107.41□)}$ =251−54.37=196.63 kJ mol^{-1}

ΔT=107.41−25=82.41□

1□=$Ea_{at\ (25\ to107.41□)}$ /ΔT

1□=54.37 /82.41=0.659 kJ mol^{-1}…………………...…. (7)

By addition 5wt% iodine to PMMA:

The temperature of chain rupture falls to 79.52□ due to addition 5wt%iodine□T_g=79.52□ (From fig.7)

Since Ea=R*T*D_f that means:

251=0.0083□352.67□D_f

D_f=85.753

ΔT=79.52−25=54.52℃

Addition $Ea_{\text{from (25 to 79.52°C+}}$5%iodine$_{)}$ =54.52℃*0.659 kJmol^{-1}

$Ea_{\text{from (25 to 79.52°C+}}$5%iodine$_{)}$ =35.928 kJ mol^{-1}

Given energy from addition 5%iodine= 54.37-35.928=18.442 kJ mol^{-1} …..(8)

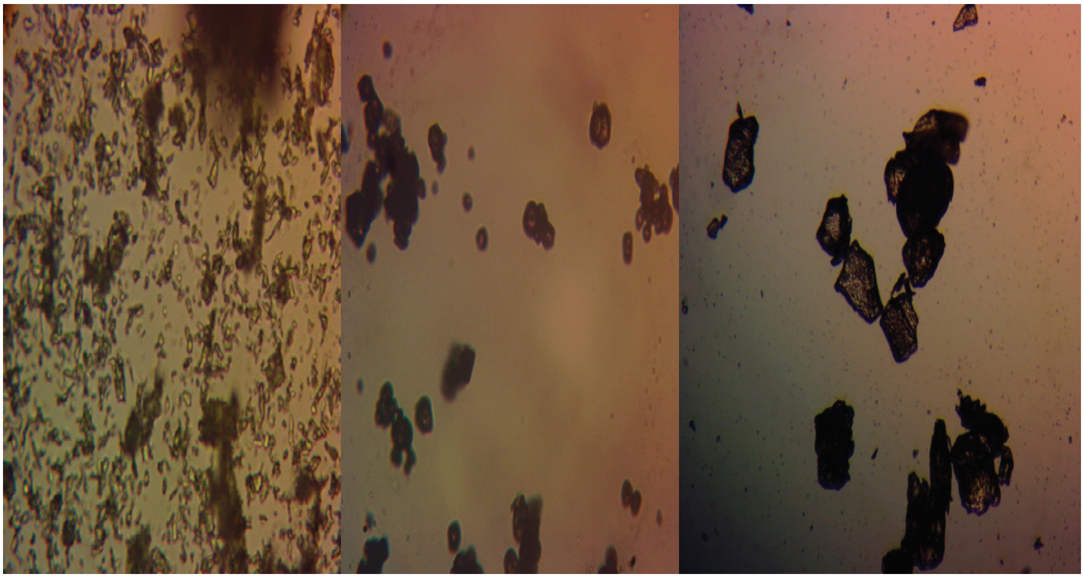
$Ea_{\text{at (79.52°C)}}$ =196.63−18.442= 178.188 kJ mol^{-1}

For other polymers and their composites, the calculations were repeated and tabulated in table 1.

Table (1): TheEffect of 5wt%iodine on usedpolymers at R.T (25°C) &Ea (251 kJ mol^{-1}) with D_f (101.43)

Substance	Tg(°C)	Df	Eaat Tg (kJ mol-1)	Addition Ea (kJ mol-1)	Given Ea from heating and addition iodine (kJ mol-1)
Pure PMMA	107.41	79.46	196.63	54.37	_
5%I2+PMMA	79.52	85.753	178.188	35.928	18.442
Pure PVA	101.18	80.8	199.95	51.05	_
5%I2+PVA	87.29	83.918	106.79	41.734	9.316
Pure PEG	63.62	89.8	222.2	28.78	_
5%I2+PEG	57.84	91.372	217.88	24.465	4.315
Pure chitosan	92.74	82.8	204.9	46.1	_
5%I2+chitosan	52.51	92.86	177.5	18.706	27.394
Pure cellulose	80.32	85.6	211.83	39.17	_
5%I2+cellulose	80.5	85.519	211.524	38.864	0
Pure starch	93.89	82.56	204.3	46.7	_
5%I2+starch	71.6	87.731	185.886	28.286	18.414

The calculations shows that addition of 5wt% I_2 causes generally in the Tg values for all polymers except cellulose. That means, that I_2 acts as plasticizer for all polymers except cellulose.



Chitosan StarchCellulose

PMMA PVA PEG

This indicate that iodine molecule diffuses through the networkof the polymers except cellulose, thus iodine rupture the engineering bonds of the polymers specially their hydrogen bonds.In case of chitosan, iodine attacks its hydrogen bonding through nitrogen and oxygen which show the highest depression in its Tg (40.23**°C**) from (92.74 to 52.51) **°C**.While cellulose not affected, it seems that cellulose molecule coated withprotective film comparing with starch where its Tg reduced from (93.89 to 71.6) **°C**.This is due to different structure of cellulose and starch as shown in fig.14 (a-b)

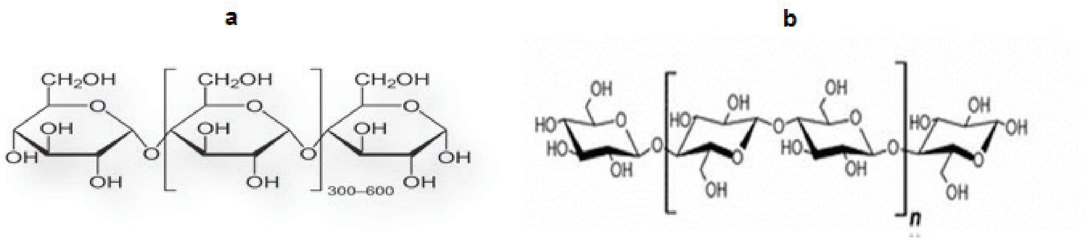


Fig.14 (a): structure of starch, (b): structure of cellulose

Also iodine colored all polymers except cellulose this support the above discussion, i.e. cellulose coated with impermeablemembrane.That proved the differences in the chemical structures between cellulose and starch. Cellulose does not dissolve by solvent, while starch dissolved, therefore cellulose undigested by the human body conditions.PMMA shows relatively highest Tg (107.41°C). This is due to the definition is basically the same as with elastomers, but instead of a chemical cross-linking there is a physical cross-linking (as shown its structure in fig.15)

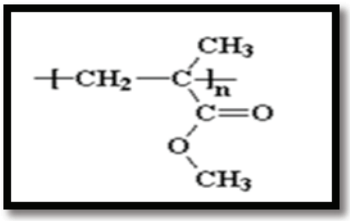


Fig (15): Structure of PMMA

and Tg above 0°C, thus it is highly affected with addition of iodine in which the Tg drop to the (79.52°C). In previous work cellulose shows drop in Tg with addition of 3%carotene, which attributed to that carotene molecule has 22delocalizedπ –electrons moving along carotene molecule which inter the fine film surrounding the cellulose molecule.This support the conclusion of the present research, that is cellulose molecule surrounding by a protective membrane. As the percent increase by to 7% show no change in the Tg due to the absence of functional groups in carotene and 3% is enough to the π –electrons to inter the cellulose molecule. For all polymers, Tg reduced by the following order: chitosan (40.23) > PMMA (27.89) > starch (22.29) > PVA (13.89) > PEG (5.78) >cellulose (0) °C

That means, there is no distinction between the behavior of natural and synthetic biopolymers. Also, it means that Tg depends on the types and number of the functional groups available in the polymer structure (as shown in fig.16

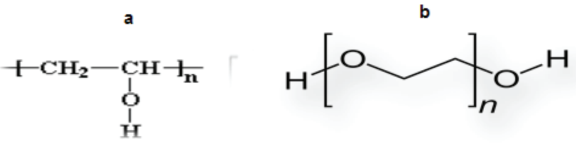


Fig. (16): a: Structure of PVA, b: Structure of PEG

As well as on their molecular weight. When comparing the chemical structures of PVA, starch and PEG, it seems that the expected destroyed hydrogen bonds is higher in PVA than starch and PEG.

In the term of energy calculations, the 5wt% I_2 addition gives highest energy to chitosan (27.394(kJ mol^{-1}) and gives no energy to cellulose and the overall ordering is:

Chitosan (27.394) >PMMA (18.442) =starch (18.414) >PVA (9.316)>PEG (4.315) >cellulose (0)

The maximum energy required to transfer polymer from its original state at RT to its state at its Tg is for PVA (41.734), while the minimum value is for chitosan (18.706). This is due to compact structure of PVA compared with the chitosan structure.

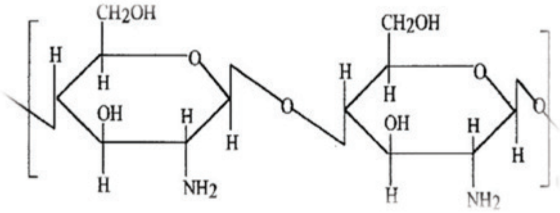


Fig. (17): Structure of chitosan

Conclusions

1- Iodine shows the highest depression in the Tg of chitosan while not effected cellulose.

2- Iodine act as inorganic plasticizer for all polymers except cellulose.

3- Iodine shows color changewith all polymers except cellulose.

4- The deepest color with starch.

5- Optical microscopy shows there is absorption of the solvent through the polymers except in case of cellulose .This indicates that cellulose molecules behave as impermeable membrane.

6- Energy calculationsshows that iodine give highest energy to chitosan (highest depression in its Tg) and zero energy to cellulose (zero change in Tg)which indicates there is two phase with cellulose –iodine system.

7- The order of decreasing Tg of polymers upon addition of 5% iodine as follow:chitosan (40.23) >

PMMA (27.89) > starch (22.29) >PVA (13.89) > PEG(5.78) > cellulose(0)

8-No distinction betweenTg of natural and industrial biopolymers.

9-Tg depends on molecular weight of polymers and on the type and number of functional groups in the polymer.

Financial Disclosure: There is no financial disclosure.

Conflict of Interest: None to declare.

Ethical Clearance: All experimental protocols were approved under the College of Materials Engineering and all experiments were carried out in accordance with approved guidelines.

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