

Thermal stability and kinetic studies of gelatin/tgs composite films

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Abstract- The composite films of gelatin and gelatin/TGS were prepared successfully by using the solvent-casting technique with different composition ratios of the two materials (2, 4, 6, 8 and 10 wt% TGS). Films exhibited similar X-ray diffraction (XRD) patterns, showing a displacement in position of the gelatin characteristic peaks. Thermal characterization was used to characterize the obtained films. Helix-coil transition and glass transition temperature were measured by differential scanning calorimetry (DSC). There is interaction between gelatin and TGS through hydrogen bond formation. Thermogravimetric analysis (TGA) was used to characterize the thermal stability of the composite films. The kinetic parameters such as activation energy, entropy, enthalpy and free energy for all the investigated samples were determined using Coats-Redfern and Horowitz-Metzger equations.

Keywords- Gelatin; TGS; XRD; DSC; TGA.

1. INTRODUCTION

Recent studies have shown that gelatin-based films with various additives have good potential for applications in a number of optoelectronic and integrated optics devices. Gelatin containing ammonium dichromate is a well-known holographic recording material and is used in some holographic recording systems [Khutorsky & Sidney, (1997)]. Gelatin-based films have been used in grating couplers [Chang (1980)], multiplexed gratings [Chen *et al.* (1989)] and optical interconnections [Chen *et al.* (1990)].

Gelatin is a relatively low cost protein, industrially produced all over the world and that have excellent film forming properties. Mainly because of that, this protein is being extensively explored in edible and/or biodegradable films production and characterization studies, pure [Sobral *et al.* (2001); Carvalho & Grosso (2004); Thomazine *et al.* (2005); Vanin *et al.* (2005); Bergo *et al.* (2006)] or blended with other biopolymers (Arvanitoyannis *et al.* 1997). However, those gelatin-based films presents the typical characteristics of biopolymer-based films made with hygroscopic plasticizers are highly affected by room conditions, mainly relative humidity. Due to hygroscopic character of this material, relative humidity changes lead to alteration of its moisture content affecting consequently the films properties, as water has a strong plasticizing effect on polymeric systems [Lim *et al.* (1999); Gontard, Guilbert & Cuq, (1998)].

Triglycine sulphate (TGS) [(NH₂CH₂-COOH)₃H₂SO₄] is one of the most extensively studied material as it possess excellent pyroelectric and ferroelectric properties. It exhibit strong absorption in most of the infrared region. The crystal structure of TGS was reported by [Hoshine *et al.* (1959)] and the Curie temperature was reported a typical second-order ferroelectric phase transition at TC=49°C [Sun *et al.* (1999)]. TGS family crystals belong to the monoclinic system with the polar point symmetry group P21 in the ferroelectric phase, spontaneous polarization Ps arises along the b-axis and P2min the Para electric phase [Alexandru *et al.* (2004)]. TGS crystal has some disadvantages due to its easy depolarization by electrical, mechanical and thermal means. In order to overcome these disadvantages and to improve the ferroelectric properties of TGS, variety of dopants such as amino acids, organic and inorganic compounds have been introduced in TGS crystal.

In this work triglycinesulphate (TGS)-gelatin films were prepared and investigated. TGS was selected because it is water soluble material simplifying the process of fabrication of the films. When gelatin is dissolved in water, a gel is formed which is a very good water absorber, a feature shared with many biological materials. The aim of this work

was to prepare gelatin-triglycine sulphate (TGS) modified films in several compositions and to analyze the effect of addition of different contents of TGS on their physico-chemical properties.

2. EXPERIMENTAL TECHNIQUES

2.1. Materials

The macromolecule used for film production was: gelatin (type B and bloom=190-200) was published by E. Merck (Darmstadt, Germany), and the average molecular weight ≈ 100.000 gm/mol. From the specifications, gelatin was composed of glycine (27%), proline and hydroxyproline (25%), glutamic acid (10%), arginine (8%), alanine (9%), aspartic acid (6%) and other amino acids (15%). The ferroelectric material triglycine sulphate (TGS) was purchased from Acros organic. Its molecular weight is 170.

2.2. Preparation of composite films

In order to obtain a film of pure gelatin, gelatin was dissolved in distilled water at temperature of 37°C with continuous stirring for 30 min. until completely dissolved, then pour it into petridishes and cooled down at room temperature. Polymer/ferroelectric composite films were prepared by weighed amount of gelatin and TGS in powder form with different concentrations 2,4,6,8 and 10wt. %TGS then dissolved them in distilled water at room temperature using magnetic stirrer. Then cast on to Petri dishes and dried at room temperature for about two or three days until the solvent completely evaporated. Films were cut to slab pieces and the thicknesses of these slabs were measured 5 or 10 times using digital micrometer. The average thickness was found of order 50 μ m.

2.3. X-ray diffraction spectroscopy

X-ray diffraction patterns were obtained using advanced refraction system XRD scintag Ins., USA. The tube used was copper radiation and the filter was nickel. The relative intensity was recorded in scattering over an angular (2θ) of 4-50 $^{\circ}$.

2.4. Thermal analysis (DSC, TGA)

Thermal analysis was carried out using a computerized differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), TA-50 Shimadzu Corporation, Kyoto, Japan. All functions were incorporated into a single compact instrument including detector, temperature, gas control and computer interface. The heating rate was programmed in steps between 0.1 and 99.9°C/min. Measurements were carried out under nitrogen atmosphere (30mL/min). The heating rate used for all samples under investigation was 10°C/min.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction

X-ray diffraction analysis has yielded a great deal of valuable information on the configuration of macromolecules and on the structure, orientation and size of ordered regions in the materials. Figure 1-a shows the typical X-ray diffraction pattern obtained for pure gelatin film measured at room temperature in the scanning range $4 \leq 2\theta \leq 50$. This spectrum is characteristic of a partially crystalline material with a broad peak located at $2\theta = 20^{\circ}$ and a small peak located in the region of $2\theta = 7-8^{\circ}$. These peaks indicate the reconstitution of the collagen like triple helix structure.

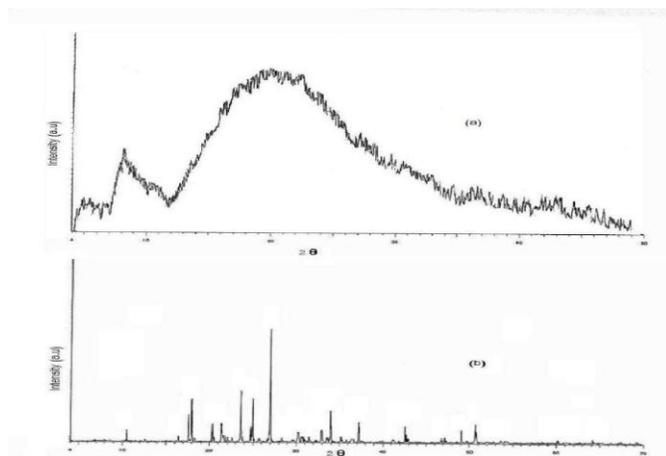


Fig. 1(a, b): X-ray diffraction patterns for (a) pure gelatine (b) pure TGS.

(Bigi et al., 2004) confirmed that the peak at 2θ around 8° is related to the diameter of the triple-helix and its intensity would be associated with the triple helix content of the films. Also, [Yakimets et al. (2005)] have studied the crystallinity of pure gelatin films and observed a characteristic peak at $2\theta=7-8^\circ$. It is reported that this peak corresponding to the presence of a small amounts of triple-helical structure, characteristic of the rod-like triple helices of collagen, with 300nm long and 1.5nm wide. This means that the crystallization of gelatin is due to its tendency to re-naturation.

Figure 1-b shows the X-ray diffraction pattern of pure TGS at room temperature in the scanning range $4 \leq 2\theta \leq 70$ indicating the different crystalline peaks. The peaks observed in the X-ray diffraction patterns for TGS crystal match well with the reported ASTM data [ASTM (1967)] and with that reported recently [Jayalakshmi & Kumar (2008); Balu et al. (2009)]. The diffractograms reveal a monoclinic structure for TGS with maximum peak corresponding to the (040) plane at $2\theta=27^\circ$.

It was expected that the X-ray diffraction patterns Figure 2 (a:e) of gelatin/TGS composite films would be of partially crystalline materials, because the films made with both pure partially crystalline and pure crystalline structure TGS. Generally, all the samples are characterized by the gelatin main characteristic peaks which located at $2\theta=20^\circ$ and $2\theta=7-8^\circ$ which shows some shift in its positions and the intensity.

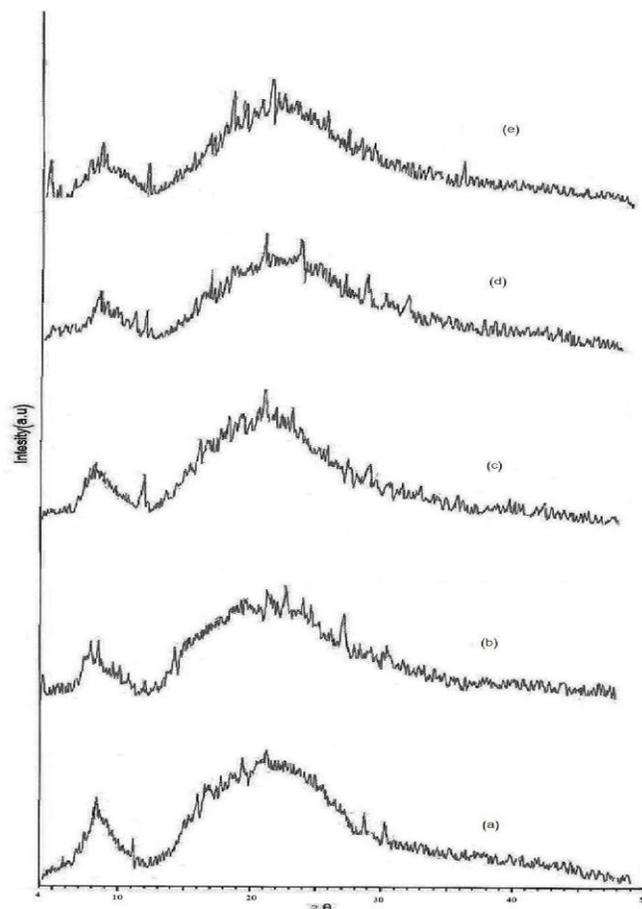


Fig. 2: X-ray diffraction patterns for (a) 2, (b) 4, (c) 6, (d) 8 and (e) 10wt. % TGS.

Also, there are new crystalline peaks appearing at different positions with different relative intensities and the triple helix structure peak belong to gelatin at $2\theta=8^\circ$ is shifted and splitted in the composite films and its intensity was very high in 2wt.%TGS composite sample. A sharp peak is detected at $2\theta=4^\circ$ for the composite sample 10wt. %TGS. There are some other new crystalline peaks at $2\theta=15^\circ$ and 29° appeared in the X-ray diffraction of the composite films. From the structural point of view, gelatin differs from other proteins due to its considerable absence of internal order and random configuration of its polypeptide chains of different amino acids. About 50% of these were polar, being ionic and 50% non ionic. Thus, half of gelatin monomers show potential to interact with other polar material such as TGS. The results confirm that an interaction through hydrogen bond occurred between the two polar materials and was due to incorporation of polar crystalline TGS into polar gelatin polymer, which leads to good compatibility between them.

3.2. Thermal analysis (DSC)

The thermal analysis provides information not only about the thermal properties but also gives clues about the structure of the materials. The DSC thermogram of gelatin film sample from room temperature up to 450°C is shown in Figure 3. At a temperature of $T \approx 54.7^\circ\text{C}$ a faint endothermic event is observed which indicates the time-dependent thermal relaxation in the gelatin polymer.

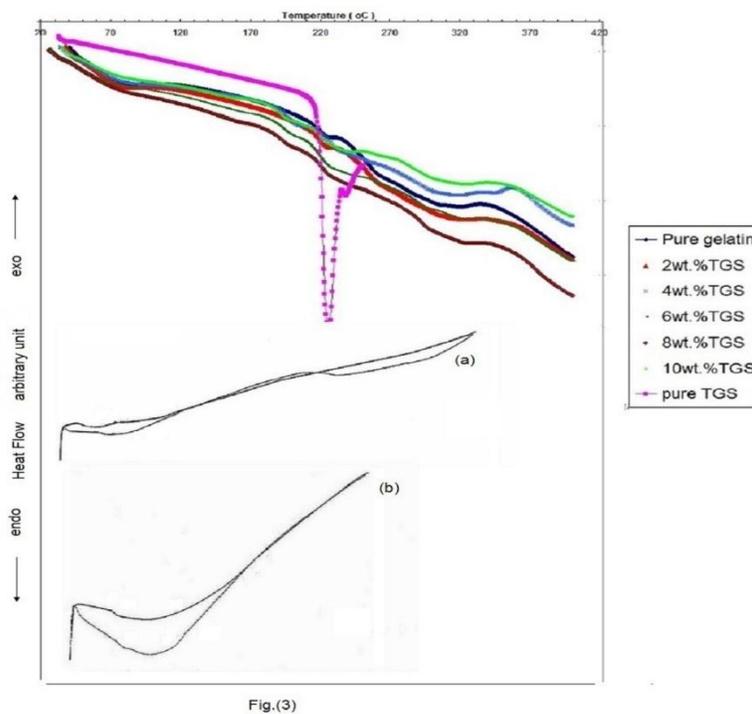


Fig. 3: DSC thermogram for pure gelatin, pure TGS , 2,4, 6, 8 and 10wt.% TGS. (a,b): The first and second heating scans of the DSC thermogram for pure gelatin and pure TGS

This transition is apparently responsible for the overall physical behavior of gelatin and the obtained value is consistent with the most cited and studied [Chen *et al.* (2005)]. This first step changes in heat flow was assigned to glass-to rubber transition T_g relating to the amorphous regions of the biopolymer, which are in glassy state at the water contents of interest at room temperature due to the micro-Brownian motion of the main backbone chain [Mousia *et al.* (2000)]. The glass transition was followed by an endothermic peak which attributed to melting of triple-helix crystalline structure. This transition is associated with melting and dissociation of the ordered regions at temperature $T_m \approx 86.2^\circ\text{C}$. Several authors attributed this endothermic peak to the overlapping of different processes such as water evaporation, melting and recrystallization of small and/or imperfect gelatin crystallites, and association of the glass transition of α -amino acid blocks in the polypeptide chain (Dai *et al.* 2006). The peak temperature, and moreover the enthalpy of this endothermic processes are strongly related to the film drying condition (preparation conditions). This effect has been studied by some authors (Dai *et al.* 2006; Ramachandran & Ramakrishnan, 1967). Another two successive endothermic peaks located at 212.4°C and 248.8°C respectively. The endothermic peak at 212.4°C is known as the decomposition temperature of gelatin [Cortesi *et al.* (1998)], such as the blocks of imino acids, proline and hydroxyproline with glycine [Yannas *et al.* (1966)]. Also, the DSC curve of gelatin show an exothermic peak at about 334.7°C , which is attributed to the disintegration of intermolecular side chain (Li *et al.* 2006). An interesting attention has been paid to a DSC thermogram of gelatin film in temperature range from ambient temperature to 300°C in such a way that after the first heating the sample was cooled at identical rate and then second heating cycle was performed (Figure_3-a). It was found that during the first scan T_g and T_m were observed at 54.7°C and 86.2°C respectively. After melting of gelatin it was cooled relatively rapidly ($10^\circ\text{C}/\text{min}$) and thus super cooled into rubbery and then the glassy state. The thermogram acquired shortly after cooling, showed only a glass-rubber transition indicating that the reordering (i.e. the reformation of gelatin helical structures and their aggregation did not take place during the time scale of the cooling process. The thermogram, therefore indicates that before the first heating scan, the gelatin films had a partially crystalline structure, while the post-cooling heating scan was performed on an essentially amorphous

polymer [Yakimets *et al.* (2005)]. The important observation was that T_g of partially crystalline gelatin is slightly higher than that of amorphous equivalent. The reduction of the T_g for gelatin indicates that the bound water was released at the end of the first heating scan. On the second heating scan, the released water plasticizes the new completely amorphous gelatin, which leads to this reduction in the T_g .

Figure 3 shows the DSC traces for the first heating scan of the powder TGS from room temperature up to 250°C. Only three endothermic peaks are observed through the studied temperature range. The first endothermic peak observed at 49.8°C with enthalpy of about 13.8J/g due to the well-known phase transition of TGS [Alexandru *et al.* (2004)]. At this Curie temperature 49.8°C TGS shows second order ferroelectric transition and it is an order-disorder ferroelectric so 49.8°C is the structural phase transition temperature T_p . The second endothermic peak at 225.8°C with the greatest enthalpy of 374.9 J/g is corresponding to the melting temperature of TGS crystalline domains. At the final stage for endothermic peak of the melting of TGS an interfering small endothermic peak at 238.2°C with enthalpy of 158.9 J/g is observed which may be due to thermal degradation has been done.

Figure 3 illustrates the DSC curves of gelatin with different concentrations of TGS (2, 4, 6, 8 and 10wt. %TGS) and how the thermal transition is varied through the range of temperature from room temperature up to 450°C with identical rate of heat (10°C/min). They showed only one T_g followed by an endothermic peak due to the ordered triple helical structure is developed in the composite samples and confirmed its existence at the melting temperature T_m , where their values depending upon the composition ratio. Also, there are two endothermic peaks appeared in the DSC thermogram and there is an exothermic peak like that found in DSC of pure gelatin at different temperatures according to the composition ratio. Table 1 summarize the values of the glass, melting temperatures and their enthalpies associated with each transition obtained through analysis of DSC curves for both pure samples and all the composite samples. From Figure 3, it was found that with increasing TGS content, the endothermic peaks transitions become quite broad and display a larger area than that found in gelatin itself. Especially in the composite sample 2wt.%TGS than the other samples. Where it has the highest values for all the recorded temperature transitions. In support of this finding the sample 2wt.%TGS in figure 4(b) is considered for DSC runs as that done in Gelatin. It is observed that the melting point increases with the addition of TGS also with increasing of enthalpy. This indicates that the crystallinity is enhanced (i.e. Gelatin crystal becomes more perfect and has higher melting point). After heating the sample is cooled with rate of 10 °C/min followed by the second heating run. Through this second heating run, no thermal melting point is detected except that T_g at a temperature lower than that observed in the first run. This suggest that during the first heating, Gelatin crystals are melted and the molten Gelatin molecules were not able to reorganized into crystalline phase in the presence of strong interacting TGS molecules upon cooling.

Table 1: Transition temperature and associated enthalpies for gelatin, TGS and their composite sample.

sample	Glass transition temperature		Melting temperature		Structure phase transition		Degradation temperatures							
	T_g (°C)	ΔH (J/g)	T_m (°C)	ΔH (J/g)	T_p (°C)	ΔH (J/g)	T_d	ΔH (J/g)	T_e (°C)	ΔH (J/g)	T_o (°C)	ΔH (J/g)	T_{10} (°C)	ΔH (J/g)
Gelatin	54.72	56.77	86.20	141.25	-	-	-	-	212.43	12.32	248.86	18.94	334.76	164.90
TGS	-	-	225.82	374.93	49.89	13.86	238.20	158.90	-	-	-	-	-	-
2wt%TGS	58.49	66.81	89.44	162.13	-	-	-	-	214.59	16.15	257.82	22.48	359.2	179.54
4wt%TGS	56.29	65.21	86.74	152.48	-	-	-	-	218.81	13.11	240.15	17.63	357.12	172.48
6wt%TGS	55.97	59.85	86.90	148.13	-	-	-	-	202.90	12.84	235.28	17.18	345.76	165.38
8wt%TGS	54.81	58.27	85.93	144.50	-	-	-	-	202.73	12.15	233.01	17.04	342.33	155.82
10wt%TGS	53.90	56.80	85.90	142.90	-	-	-	-	200.40	11.43	231.17	16.44	339.47	142.39

Crystallinity percentage variation ($\Delta\chi$) is calculated by the following equation [Fintzou (2006)]

$$\Delta\chi = \frac{\Delta H^* - \Delta H}{\Delta H} \times 100, \quad (1)$$

Where, ΔH^* is the fusion enthalpy of composite sample and ΔH is the fusion enthalpy of Gelatin. Fusion enthalpy ΔH^* related to crystallinity, it reaches its maximum value for the composite sample 2wt%TGS and then decreases in some way to be 7.6, 4.77, 1.99 and 0.53 for the composite samples respectively.

3.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is considered the most practical widely used method to illustrate the thermal stability of the material over a wide range of temperature. The shape of the curve of TGA and its derivative DTG depends primarily upon the kinetic parameters involved.

Figure 4(a,b) shows a typical TGA(4-a) thermogram and their derivatives DTG(4-b) for gelatin, TGS and their composite ratios. TGA curves (4-a) were analyzed as percentage weight loss as a function of temperature in the range from the ambient temperature up to 500°C. The decomposition stages, temperature ranges of decomposition, maximum decomposition peak temperature of the DTG percentage losses in mass are given in Table (2). From the graph it appears that gelatin decomposes via two stages [Chen *et al.* (2005)] over the temperature from room temperature up to 500°C.

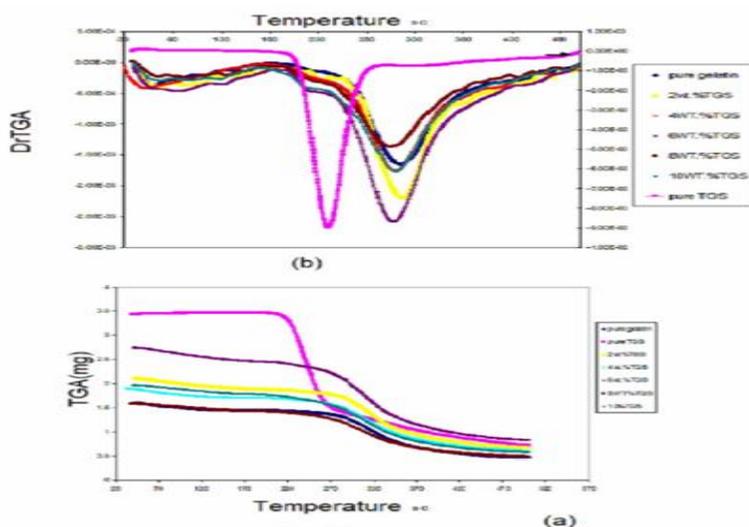


Fig.4.(a,b):TGA and DTG for pure gelatin, pure TGS and all the composite samples 2,4,6,8 and 10 wt%TGS.

The first step occurs within the range 50-150°C with mass loss of (9.90%) which may be due to the moisture vaporization. The second occurs within the range of 220-320°C with a mass loss (61.24%) which may be due to loss of ammonia and the thermal degradation of gelatin molecule [Chen *et al.* (2008)]. From the corresponding DTG curve (4-b) of gelatin, two endothermic peaks have their maximum at 59°C and 314°C respectively. Which is in good agreement as previously reported.

Pure TGS crystals showed a major weight loss (49.0%) in the temperature range between 218-268°C. This can be attributed to the decomposition of glycine into CO_2 and NH_3 . Further increase in temperature result in the removal of H_2SO_4 in the form of H_2O and SO_3 with a total mass loss of (20.0%) at temperature range 300-499.9°C. From the corresponding DTG curve of TGS crystal also showed a sharp peak at 240°C and another peak at 490°C which is in agreement with that reported by (Parimaladevi *et al.* 2010).

Also, Figure 4(a,b) show a typical TGA thermogram and their derivatives DTG for (2, 4, 6, 8 and 10wt. %TGS). We notice that the composites show different behaviors, where the peak temperature T_p in the first region are more higher than that detected for gelatin but still with lower mass loss. However, the lower values of the mass loss as seen in Table(2) in the first decomposition step may be due to splitting or volatilization of small molecules and/or

evaporation of residual absorbed water. The second step in TGA analysis covers a wide range of temperature including the melting temperature of gelatin as physical transition and the thermal degradation processes where the higher values of mass loss is detected such as the loss of ammonia and water via imidization and dehydration respectively. It is important to mention that the third region was detected for all the studied composite samples of the different composition of TGS. This means that the decomposition of H_2SO_4 from the lattice of TGS in the composite sample retains its characteristic of decomposition at the temperature around $490^\circ C$ as will be seen from the studying of the derivative TGA. From Figure (4-b) of DTG curves, the peak temperature T_p of the main degradation step in the second decomposition region is shifted to lower temperature for the most composite samples as compared to the corresponding T_p value of pure gelatin. The only exception case is found in 2wt.%TGS that has higher peak temperature. Since the second region indicate chemical bond scission and backbone or branches degradation. Accordingly, it is possible to say that the sample 2wt.%TGS is more stable or there is an improvement in its thermal stability while the other composite samples are still less thermal stable. Thus, the chemical structure of the composites has been done through different stages of reactions and plays an important role in the thermal decomposition processes. Therefore, the addition of TGS to gelatin films enhances their thermal stability in general.

Table 2: Thermal decomposition of gelatin, TGS and their composite samples.

Sample	steps	Temp.range ($^\circ C$)	DTG peak ($^\circ C$)	TG weight loss (%)
Gelatin	1st	41.89 – 206.26	59.00	9.90
	2nd	207.36 – 499.75	314.53	61.24
TGS	1st	180.0 – 270.0	240.0	49.00
	2nd	300.0 – 499.9	490.0	20.00
2wt.%TGS	1st	41.90 – 225.72	66.64	12.02
	2nd	226.68 – 350.0	318.03	56.01
	3rd	350.0-499.9	487.0	17.30
4wt.%TGS	1st	31.77 – 176.27	64.44	10.20
	2nd	176.27 – 350.0	310.04	57.46
	3rd	350.0 – 499.9	485.0	18.00
6wt.%TGS	1st	42.0 – 176.17	65.47	10.24
	2nd	176.17 – 350.0	306.99	59.23
	3rd	350.0 - 499.9	485.0	19.20
8wt.%TGS	1st	38.86 – 176.71	64.33	9.35
	2nd	177.78 – 350.0	305.76	60.10
	3rd	350.0 – 499.9	486.0	19.85
10wt.%TGS	1st	40.84 – 172.41	66.64	9.10
	2nd	172.41 – 350.0	310.06	61.46
	3rd	350.0 – 499.9	487.0	21.13

3.4. Kinetic studies:

Several equations have been proposed as means of analyzing a TG curve and obtaining values for kinetic parameters. Many authors (Coats & Redfern, 1964; Horowitz & Metzger 1963) have discussed the advantages of this method over the conventional isothermal method.

3.4.1. Coats-Redfern equation:

The Coats-Redfern equation, which is a typical integral method, can be represented as:

$$\int_0^{\infty} \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\alpha} \int_{T_1}^{T_2} \exp\left(\frac{-E^*}{RT}\right) dt \quad (2)$$

as mentioned before that α is the fraction decomposed at time t , n is the order of the reaction, R is the gas constant in ($\text{J mol}^{-1}\text{K}^{-1}$), T is the peak temperature and E^* is the activation energy.

For convenience integration the lower limit T_1 is usually taken as zero, this equation on integration gives.

$$\ln\left[-\ln(1-\alpha)/T^2\right] = -\frac{E^*}{RT} + \ln[AR/\phi E^*] \quad (3)$$

A plot of the left-hand side (LHS) against $1000/T$ was drawn for both pure samples and all the composite samples and presented in Figure 5 (a) of the Coats-Redfern plots of the first, second and third decomposition steps for both pure samples and 2wt% TGS as representative of the composite samples. E^* is the activation energy in (kJ mol^{-1}) and calculated from the slope and A (in sec^{-1}) from the intercept value. The entropy of activation in ($\text{J K}^{-1} \text{mol}^{-1}$) was calculated by using the equation:

$$\Delta S^* = R \ln\left(\frac{Ah}{K_B T}\right) \quad (4)$$

Where K_B is the Boltzmann constant, h is the Plank's constant and T is the DTG peak temperature (Flynn & Wall, 1996).

$$\Delta H^* = E^* - RT \quad (5)$$

$$\Delta G^* = \Delta H^* - T\Delta S \quad (6)$$

The calculated values of E^* , A , ΔS^* , ΔH^* and ΔG^* for the decomposition steps are given in Table 3.

3.4.2. Horowitz- Metzger equation:

The Horowitz-Metzger equation is an illustrative of the approximation methods. For a first-order kinetic process the Horowitz-Metzger equation may be written in the form:

$$\log\left[\log\left(\frac{w_\alpha}{w_\gamma}\right)\right] = \frac{E^* \theta}{2.303RT_s^2} - \log 2.303 \quad (7)$$

Where T_s is the DTG peak temperature, T is the temperature at time t , $\theta = T - T_s$,

$w_\gamma = w_a - w$, w_a = mass loss at the completion of the reaction; w = mass loss up to time t . The plot of $\log [w_\alpha / w_\gamma]$ versus θ was drawn for both pure samples and 2wt% TGS as representative of the composite samples. Figure 5 (b) represent the Horowitz-Metzger plots of the first, second and third decomposition steps. It is found that E^* was calculated from the slope of the fitted linear plot.

The pre-exponential factor, A, was calculated from the equation:

$$\frac{E^*}{RT_s^2} = \left[\frac{A}{\phi \exp(-E^* / RT_s)} \right] \quad (8)$$

The thermodynamic parameters as the entropy of activation ΔS^* , the enthalpy of activation ΔH^* and Gibbs free energy, ΔG^* were calculated and given in Table 3.

Table 3: Thermodynamic data of thermal decomposition of gelatin, TGS and their composites.

Sample	stage	Method	E [#] (KJ/mol)	ΔS [#] (J/Kmol)	ΔH [#] (KJ/mol)	ΔG [#] (KJ/mol)	R	
Gelatin	1 st	CR	41.35	-214.23	38.59	109.71	0.994	
		HM	40.52	-163.65	37.76	92.09	0.998	
	2 nd	CR	50.93	-174.04	46.04	148.34	0.999	
		HM	57.49	-199.56	52.60	169.74	0.992	
TGS	1 st	CR	223.50	41.94	219.24	240.75	0.976	
		HM	164.78	36.32	160.52	179.15	0.997	
	2 nd	CR	9.91	-98.63	3.56	78.82	0.999	
		HM	41.12	-252.43	34.75	227.38	0.992	
2wt.% TGS	1 st	CR	38.48	-204.97	35.64	105.12	0.992	
		HM	37.53	-176.76	34.70	94.73	0.993	
	2 nd	CR	49.21	-183.79	44.28	152.90	0.999	
		HM	51.49	-211.46	46.57	171.54	0.996	
		3 rd	CR	8.57	-99.54	2.25	78.00	0.999
			HM	16.58	-291.97	10.26	232.45	0.988
4wt.% TGS	1 st	CR	35.25	-204.36	32.55	98.77	0.981	
		HM	35.86	-176.09	33.16	90.28	0.992	
	2 nd	CR	41.88	-172.06	37.03	137.34	0.999	
		HM	51.25	-209.84	46.41	168.74	0.998	

	3rd	CR	9.52	-97.47	3.20	77.18	0.998
		HM	18.74	-288.08	12.43	231.37	0.999
6wt.% TGS	1 st	CR	34.74	-199.13	31.76	103.05	0.997
		HM	34.18	-187.12	31.20	94.54	0.993
	2 nd	CR	36.70	-170.82	31.88	130.79	0.998
		HM	51.19	-209.18	46.38	167.49	0.998
	3rd	CR	9.87	-96.52	3.49	76.84	0.999
		HM	22.05	-282.35	15.74	230.32	0.999
8wt.% TGS	1 st	CR	33.78	-194.02	30.97	96.36	0.990
		HM	33.76	-188.09	30.95	94.43	0.996
	2 nd	CR	37.87	-156.63	33.06	123.59	0.998
		HM	50.38	-210.52	45.58	167.26	0.997
	3rd	CR	9.99	-96.23	5.18	60.90	0.999
		HM	21.00	-284.14	14.68	230.91	0.995
10wt.% TGS	1 st	CR	31.91	-133.86	29.09	74.47	0.995
		HM	35.10	-183.86	32.28	94.61	0.977
	2 nd	CR	30.54	-155.02	25.69	116.07	0.999
		HM	51.25	-210.20	46.40	168.94	0.996
	3rd	CR	10.19	-95.79	3.88	76.68	0.999
		HM	21.06	-284.17	14.73	231.27	0.996

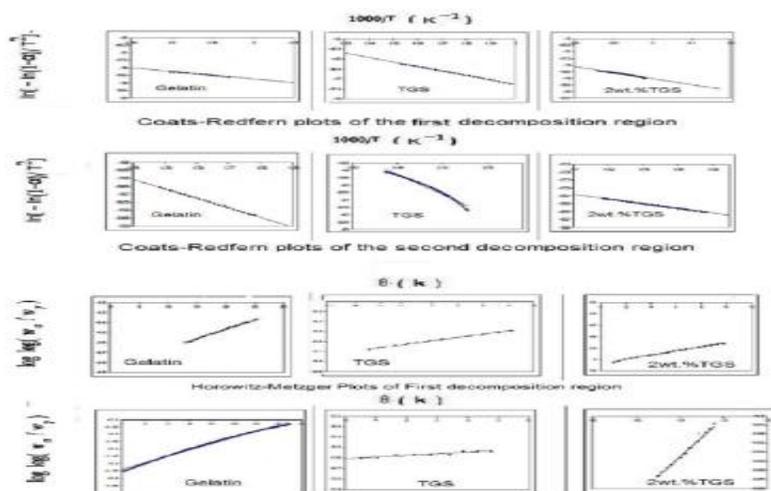


Figure 5(a,b): (a) Coats-Redfern plots of the first, second and third decomposition steps for pure gelatin , pure TGS and 2wt.%TGS. (b)Horowitz-Metzger plots of the first , second and third decomposition steps for pure gelatin , pure TGS and 2wt.%TGS.

4. CONCLUSIONS:

From the foregoing results; the following conclusions may be formulated:

1-Results data revealed that the incorporation of TGS molecules into Gelatin was achieved. The interaction mechanism could be occurred between Gelatin and TGS through the free chains of the ionic polar components of the two materials, the helical components of Gelatin with free water molecules.

2- The X-ray diffraction (XRD) results confirm the structural change in Gelatin and an increasing of its crystallinity due to the incorporation of TGS into it.

3-Thermal scanning calorimetry (DSC) analysis showed that the composition films have glass transition temperature higher than Gelatin and indicate the phase temperature and degradation processes.

4- Judging from both X-ray spectra and the increased values of T_m in DSC scan for the composite samples, it may be presumed that the crystallinity of Gelatin is increased by the incorporation of TGS. Also, the calculation of degree of crystallinity using DSC enthalpies confirms the increasing of crystallinity.

5-Thermogravimetric (TGA) data obtained with the two methods are in harmony with each other. The higher values of activation energies of the Gelatin/TGS composite films led to thermal stability of the studied composites. TGA analysis showed that the addition of TGS to Gelatin enhanced the thermal stability and the values of activation energies changes with increasing TGS content. Where the most stable composite was found for 2wt.%TGS sample.

REFERENCES:

- Alexandru, H.V. ; Berbecaru, C. ; Stanculescu, F. ; Pintilie, L. Matei, I & Lisca, M. (2004). Doped TGS crystals for IR detection and sensors. *Sensors and Actuators A*, **113**, 387-392.
- Arvanitoyannis, I. ; Psomiadou, E. ; Nakayama, A. ; Aiba, S. & Yamamoto, N.(1997). Edible film made from gelatin, soluble starch and polyols. *Food Chemistry (Part 3)*, **60**, 593-604.
- Balu, T. ; Rajasekaran, T.R. & Murugakoothan, p.(2009). Studies on the growth, optical and mechanical properties of ADP admixed TGS crystals. *Current Applied Physics*, **9**, 435-440.
- Bergo, P.V.A.; Carvalho, R.A. ; Sobral, P.J.A. ; Bevilacqua, F.R.S. ; Pinto, J.K.C. & Souza, J.P.(2006). Microwave insertion loss measurements in gelatin-based films. *Measurement Science and Technology*, **17** (12), 3261-3264.
- Bigi, A. ; Panzavolta, S & Rubini, K.J.(2004). Relationship between triple helix content and mechanical properties of gelatin films. *Biomaterials*, **25**, 5675-5680.

- Carvalho, R. A. & Grosso, C.R.F. (2004). Characterization of gelatin based films modified with transglutaminase, glyoxal and formaldehyde. *Food Hydrocolloids*, **18**, 717-726.
- Chang, B.J.(1980). Dichromated gelatin holograms and their applications. *Optical Engineering*, **19**, 642-648.
- Chen, C-H. ; Wang, F-Y. ; Mao, C-F. ; Liao, W-T. & Hsieh, C-D.(2008). Studies of chitosan: II. Preparation and characterization of chitosan/polyvinyl alcohol/gelatin ternary blend films. *Biological Macromolecules*, **43**, 37-42.
- Chen, R.T. ; Phillips, W. ; Jansson, T. & Pelka, D. (1989). Integration of holographic optical element with polymer gelatin waveguide on GaAs, LiNbO₃, glass and aluminium. *Optics Letters*, **14**, 892-894.
- Coats, A.W. & Redfern, J.P. (1964). Kinetic parameters from thermogravimetric data. *Nature*, **201**, 68-69.
- Cortesi, R. ; Nastruzzi, C. & Davis, S. (1998). Sugar cross-linked gelatin for controlled release: microspheres and disks. *Biomaterials*, **19**, 1641-1649.
- Cristina, P. ; Koro, K.L.C. ; Arantxa, E. ; Roxana, R. & Mondragon, I.(2010). Enhancing water repellence and mechanical properties of gelatin films by tannin addition. *Bioresource Technology*, **101**, 6836-6842.
- Gontard, N. ; Guilbert, S. & Cuq, J.L.(1997). Proteins as agricultural polymers for packaging production. *Cereal Chemistry*, **75**(1), 1-9.
- Horowitz, H.W. & Metzger, G. (1963). A new analysis of thermogravimetric traces. *Anal Chemistry*, **35**, 1464-1468.
- Hoshino, S. ; Okaya, Y. & Pepinsky, R. (1959). Crystal structure of the ferroelectric phase of (glycine)₃.H₂SO₄. *Physics Rev.*, **115**, 323-330.
- Jayalakshmi, D. & Kumar, J. (2008). Growth and characterization of l-tryptophan-doped ferroelectric TGS crystals. *Crystal Growth*, **310**, 1497-1500.
- Khutorsky, V. E. & Sidney, B. Lang. (1997). Very strong influence of moisture on pyroelectric and dielectric properties of triglycine sulfate-gelatin films. *Applied Physics*, **82**, 1288-1292.
- Lal, R.B & Batra, A.K.(1993). Growth and properties of triglycine sulphate (TGS) crystals. *Ferroelectrics*, **142**, 51-55.
- Li, B.; Kennedy, J.F. ; Jiang, Q.G. & Xie, B.J.(2006). Quick dissolvable, edible and heatsealable blend films based on konjac glucomannan-gelatin. *Food Research International*, **39**, 544-549.
- Meera, K. ; Claude, A. ; Muralidharan, R. ; Choi, C.K. & Ramasamy, P.(2005). Growth and characterization of EDTA-added TGS crystals. *Crystal Growth*, **285**, 358-364.
- Ramachandran, G.N. ; Ramakrishnan, C. In *Biochemistry of Collagen*; Ramachandran, G.N. ; Reddi, A.H. , Eds.;Plenum:New York, (1967).
- Sobral, P.J.A. ; Menegalli, F.C. ; Hubinger, M. D. & Roques, M. A.(2001). Mechanical, water vapor barrier and thermal properties of gelatin based edible films. *Food Hydrocolloids*, **15**(4-6), 423-432.
- Sun, D. ; Yu, X. & Gu, Q.(1999). Growth kinetics and mechanism of TGS crystals. *Res.Technol.*, **34**, 1255-263.
- Thomazine, M. ; Carvalho, R.A. & Sobral, P.J.A. (2005). Properties of gelatin films plasticized by blends of glycerol and sorbitol. *Food Science*, **70**, 172-176.
- Yakimets, I. ; Nikolaus, W. ; Andrew, C.S. ; Reginald, H.W. ; Farhat, I. & Mitchell, J. (2005). Mechanical properties with respect to water content of gelatin films in glassy state. *Polymer*, **46**, 12577-12585.
- Yakimets, I. ; Paes, S.S. ; Nikolaus, W. ; Andrew, C.S. ; Reginald, H.W. ; Farhat, I. & Mitchell, J. (2007). Effect of water content on the structural reorganization and elastic properties of biopolymer films: a comparative study. *Biomacromolecules*, **8**(5), 1710-1712.