

## Research Article

# Affect the Cross Linking Degree and Polymer Composition on the Mechanical Properties of Poly (vinyl alcohol)/ Pullulan Films

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### Abstract

In this study Cross-linked PVA/Pullulan film was prepared. Cross-linking reaction done by addition of glutaraldehyde at different reaction time (10,30and 60) min. Chemical interaction, mechanical, thermal properties, water solubility and film morphology was studied for cross-linked PVA/Pullulan, PVA and Pullulan only. Thus FTIR investigated formation of hydrogen bonding between pullulan and PVA with (GA). Tensile strength, tensile modulus and elongation (%) at break for PVA/Pullulan film was improved with addition of (GA) as the reaction time proceed equivalent with increasing PVA content.

**Keywords:** Polymer Film, Blend, Mechanical Properties, Crosslinking Reaction.

### الخلاصة

في هذه الدراسة تم تحضير الغشاء البوليمري المكون من خلط كل Poly (vinyl alcohol) و Pullulan بنسب وزنيه معينه. تفاعل الارتباط التشابكي تم باضافة العامل الربط (GA) و تم التفاعل بفترات زمنية مختلفة تراوحت بين 10 و 30 و 60 دقيقة. تمت في هذا البحث دراسة تأثير اضافة عامل الترابط التشابكي على العديد من الخصائص الفيزيائية والكيميائية للغشاء البوليمري قبل وبعد اجراء عملية الترابط. حيث تمت دراسة كل من طبيعة الترابط الكيميائي و الخواص الميكانيكية والحرارية وقابلية الذوبان في الماء بالاضافة الى الخصائص المظهرية لسطح الغشاء. حيث اظهرت نتائج FTIR تكون اواصر هيدروجينه بين كل من Poly (vinyl alcohol) و Pullulan نتيجة اضافة العامل الربط ادت الى زيادة التجانس بين البوليمرين. كما ان وجود العامل الربط والزيادة الوزنيه المضافة من Poly (vinyl alcohol) ادت الى تحسنا في الصفات الميكانيكية والتي شملت كلا من [Tensile strength, tensile modulus elongation (%)] للغشاء البوليمري.

## Introduction

In recent times, biodegradable polymer has "innovated in biomedical" concept. Introducing of natural polymers results in a biocompatible material with lower mechanical properties. An individual approach to produce biocompatible material with good mechanical properties was to blend biodegradable synthetic polymer with natural polymers as reinforcement agent. [1]. Miscibility is the most significant property of a blending polymer since it affects the morphology and the mechanical properties. Polymer blends are physically mixture of different structural polymers that interact by secondary forces [2]. Such as charge-transfer complexes, dipole-dipole forces and hydrogen bonding to form homogenous polymer mixtures [3] [4] [5]. Addition of cross-links among polymer chains have an effect on

the physical properties such as decrease in the viscosity, Increased Tg, increase strength ,toughness and insolubility of the polymer depending upon the degree of cross linking and presence and absence of crystallinity. Moreover, polymers insolubility was increase [6]. Cross linking can be done by different techniques according upon the structure of the polymer. One of these methods for cross-linking is the polymerization of monomers with functionalities or through irradiation, chemical reactions by adding different chemicals with heating and, sometimes, pressure. In all cases, the chemical structure of the polymer is altered through the cross linking process. [7] [8]. In the chemical cross-linking polymers are cross-linked with many chemical compounds such as glutaraldehyde, formaldehyde, epoxy compounds, dialdehyde [9]

[10] [11]. Pullulan is a water soluble extracellular polysaccharide [12]. Biocompatible, non-toxic, colorless, tasteless, can form transparent and glossy films [13]. Poly (vinyl alcohol) is a biodegradable, biocompatible and water soluble synthetic polymer, material. by reason of its has number of  $-OH$  group in each repeating unit, PVA shows a hydrophilic and able to form cross linked film via hydrogen bonding [14] [15] In this study mechanical properties of natural polymer pullulan were improved by blending with PVA. Cross linker glutaraldehyde was introduced to improve miscibility between PVA and pullulan. Effecting of cross-linking reaction on the chemical structure, degree of swelling, film morphology thermal and mechanical properties to the different PVA/pullulan ratios at different time of reaction was studied

## Materials and Methods

Pullulan was obtained by Shandong Freda Biotechnology, China. Poly (vinyl alcohol) (PVA) average MW  $\approx 31,000$ - $50,000$  with 98-99% hydrolyzed was achieved from Aldrich, Germany. Glycerol was acquired from Aldrich, Germany. 25% Glutaraldehyde (GA) aqueous solution was acquired from Aldrich, Germany.

### Preparation of Pullulan /PVA Blend Films

Preparations of Pull/PVA blend films were done by mixing Pullulan and PVA in 100ml DW at various Pullulan/PVA 100/0, 85/15, 70/30, 55/45, 40/60, 25/75 and 0/100 (wt %). Polymer mixture was stirred at  $80^{\circ}C$  to be dissolved. Then glycerol 1.19 ml was added to the polymer solution as plasticizer. The Cross linking blend film were prepared by adding 10% (v/v) HCl and 0.0001% (v/v) GA to 20 mL form Pullulan /PVA blend solutions and stirred for 10, 30 and 60 min at room temperature. Pullulan/PVA blends before and after cross linking solution were poured on a petri dish and the films were cast by drying at  $45^{\circ}C$  for 72 hr.

### Characterizations of the Blend Film

FTIR spectrum of KBr pellets for film was studied with Mattson Satellite 5000 spectrophotometer. The tensile strength, E-modulus, and % elongation at break of the polymer films with and without cross linker measured at room tem-

perature on a tensile test machine Jinqiao, China. The rectangular specimens with about (width 12.6, thickness 0.10 and length 60.0) mm mounted between the grips of the machine before applying the stress at a 40.599 N.

The polymer blend specimens were observed under a (Stereoscan 360, Cambridge) scanning electron microscope (SEM) in order to explore surface properties.

Water up take behavior of the pullulan/PVA with 75% PVA (Wt %) films only and with different cross-linking reaction time (10, 30 and 60 min) was studied at room temperature by immersing a bout ( $25 \times 25 \times 0.1 \text{ mm}^3$ ) from weighed and dry samples of the films in distilled water. The strips were removed from water at different time intervals and weighed after blotting out the excess water from the surface of the films with filter paper. The percent water absorption was calculated using the following equation:

$$\% \text{ Water Absorptivity} = ((D_s - D_d) / D_d) \times 100.$$

Where  $D_d$  and  $D_s$  are the weight of the blend films in the dry and swollen states respectively. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis ((TGA) have been done at university of Baghdad / college of education for pure sciences Ibn Al-haitham -Central service laboratory. Heating temperature was started from 0 to  $300^{\circ}C$ . With heating rate  $10^{\circ}C$  per minute. Study was done with 20 mg from PVA/Pull and crosslinking PVA/Pull with 75% PVA (Wt %).

## Results and Discussion

### Fourier Transform Infrared (FTIR)

Cross-linking reaction between pullulan /PVA blend film and the cross linker was investigate by using FTIR spectroscopy. Cross linking reaction was done when aldehyde groups of the glutaraldehyde reacted with the hydroxyl groups for both pullulan and PVA. The spectra of pure films for pullulan and PVA and cross linked blend pullulan /PVA were compared to study the effecting of cross linking reaction at different period of time on the pullulan/PVA miscibility. Figure 1 (a, b and c) present the FTIR spectra for pure pullulan, pure PVA and cross-linked blend pullulan/PVA films respectively. Figure 1 (a) shown abroad  $-OH$  band at  $3418 \text{ cm}^{-1}$ . Moreover, Characteristic polysaccharide band was found at  $1423 \text{ cm}^{-1}$ . Strong band was found at

1158  $\text{cm}^{-1}$  related to C-O-C polysaccharide ring. While in Figure (c) - OH band for PVA film was found at 3437  $\text{cm}^{-1}$  and Characteristic absorption peak for C-O stretching appears at 1044  $\text{cm}^{-1}$  and 1444  $\text{cm}^{-1}$ . However, in Figure (c) - OH stretching was shifted to lower intensity and appears at  $\text{cm}^{-1}$  by blending pullulan with PVA and cross linking with (GA). Thus it can be related to the formation of hydrogen bond between pullulan and PVA with (GA). Therefore, the FTIR spectroscopy results confirm the reaction between PVA and Pullulan.

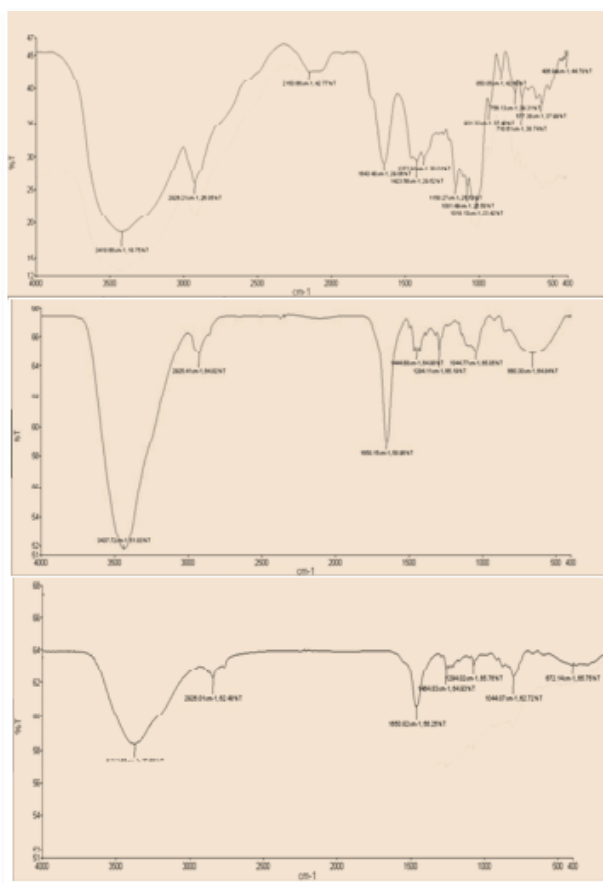


Figure 1: FTIR Spectroscopy for Pure Pullulan Film (a), Pure PVA Film (b) and Cross Linked Pullulan/PVA Film (c).

### Mechanical properties

Studies of mechanical behaviors of polymer films are very essential for the reason that they show the film applications. The mechanical properties of pullulan/PVA blend films with (0, 15, 30, 45, 60, 75 and 100) PVA (Wt %) contents were studied before and after cross linking with

(GA) at 10, 30 and 60 min. The tensile strength, tensile modulus and elongation (%) was shown in Figure 2 (a, b and c) respectively. Figure 2(a,b) show the lowest values of tensile strength and tensile modulus at lowest PVA contents of 15 and 30 wt%, respectively. The tensile strength and modulus of the blend films were increased at lower pullulan contents. Thus, it can be correlated to weakness mechanical properties of pure pullulan film such as other polysaccharide that form a slight brittleness polymer film. Lower mechanical properties for pullulan were confirmed to study done by [16] [17] As a result, by increasing the PVA contents in the blend film the (%) elongation at break decreasing as present in the Figure 2 (c). This can be attributed to the semi-crystalline structure of PVA [6]. Mechanical properties for pullulan/PVA blend film cross linked with (GA) at 10, 30 and 60 min in (a) tensile strength, (b) tensile modulus and (c) elongation (%) at break were shown in Figure 3. It was found after incorporating (GA) and increasing cross-linking reaction time from 10 min to 60 min both tensile strength and tensile modulus were increasing equivalent with increasing PVA content. Therefore, by addition of (GA) to the polymer blend miscibility was improved due to increase the hydrogen bond interaction among pullulan and PVA via (GA). As a result by increasing the cross linking reaction time the interaction was improved parallel with improved both tensile strength and tensile modulus. [19] While, (%) elongation at break decreased due to increase the interaction between these polymer reduce the brittleness of polymer film. Moreover, Figure 3 was shown by addition of (GA). The tensile properties of pullulan/PVA were improved comparing to the results of the tensile properties before cross-linking reaction as shown in Figure 2. It was found the maximum tensile strength and tensile modulus about 82 and 4000 MPa respectively at 75% PVA Wt% content. However, at same PVA content the maximum tensile strength was found about 86.89 and 89.9 MPa and tensile modulus start from 4020, 4100 to 4387 MPa at 10, 30 and 60 min respectively. Thus above results were supported with above FTIR results.

### Scanning electron microscopy (SEM)

The surfaces micrographs of the pure pullulan film ,pure PVA film, PVA /Pullulan blend film with compositions of 75% PVA (Wt%) without cross linker and PVA /Pullulan blend film with compositions of 75% PVA (Wt%) and cross linked with (GA) at 30 min was shown in Figure.4 (a,b,c and d) respectively. The pure PVA and pullulan film shows a continuous phase as shown in Figure 1a and 1b respectively Figure 1c PVA /Pullulan film illustrate a co-continuous phase separation from PVA and pullulan particles. Moreover the presence of interfaces domain and empty spaces is apparent in the micrographs of the PVA /Pullulan film, which are due to the weak interactions between PVA and pullulan. In Figure (d) homogeneity was improved, as a result of cross linking reaction and continuous phase was found from PVA/pullulan film with (GA) as crosslinker.

### Water up Take Behavior

The water up take of the dried PVA/ pullulan at 75% PVA (wt %) films only and with different cross-linking reaction time was shown in Figure 6 (a and b). As shown in these Figures, the swelling degree of the polymer decreased with the increase in cross-linking reaction time. As conferred previous, at increases time of cross-linking reaction the density of cross-linking produced increases while the intermolecular space is freely decreases. The latter is up taking within the polymer film matrix when it is in contact with water. Pure pullulan film is not showing any swelling behavior as a result of its water soluble polysaccharide [12]. Blending pullulan with PVA water resistance properties was improved, thus related to the crystallinity stature of PVA as shown in Figure 5. When (GA) was introduced with PVA /pullulan matrix, the swelling behavior was improved due to the presence of (GA) introduce cross-linking points between PVA and pullulan in film sample and therefore, less -OH groups which reduce the hydrophilicity are predictable. [18].

### Thermal properties

DSC and TGA were achieved for the Pull/PVA and pull/PVA cross linked with GA, shown in Figures (5) and (6). Thermogram measurement was performed to find out the thermal stability of polymer film. First loss in mass of Pull/PVA and cross linked Pull/PVA was due the water loss at

127 °C and 230°C respectively TGA curves demonstrated that pull/ PVA cross linked with GA was stable up to 230°C with 36.2 % mass loss occur above 303°C. Thus, pull/ PVA showed 49.1% mass loss occur above 300°C. Cross linked Pull/PVA showed higher thermal stability model, it specifies that cross-linking between the PVA and pullulan increase the thermal stability of PVA. The DSC thermogram of pull/PVA shows endothermic peak at 86.1°C can be attributed as T<sub>g</sub> of PVA followed by melting of the crystalline portion start at 195.6°C that is T<sub>m</sub> melting temperature of PVA as shown in Figure 6. The values of T<sub>m</sub> and T<sub>g</sub> are in concurrence with those in previous report (19) above results indicating that this blend was phase-separated and that the interfacial adhesion between PVA and pullulan was poor. DSC thermograms of Pull/PVA cross linked formulations showed two major endothermic peaks. However peak at 101°C can be attributed as T<sub>g</sub> for pull/PVA crosslinking with GA. Shifting in T<sub>g</sub> to higher value 101 °C can be related to the intermolecular crosslinking modifies the stuffing of local molecular, ensuing decline in free volume, then increase in T<sub>g</sub>. Moreover as a result of crosslinking reaction hindrance to the chain orientation can form elastic polymer having lower melting point. [20]

### Conclusions

In this study PVA/pullulan films was prepared both mechanical and thermal properties, water solubility of pullulan were improved via blending with PVA. We found addition of (GA) to the polymers blend produce humongous polymer film rather than film PVA/pullulan without cross-linker. Above results indicate that cross-linking is effective way for improving physical properties of polymer blend film.



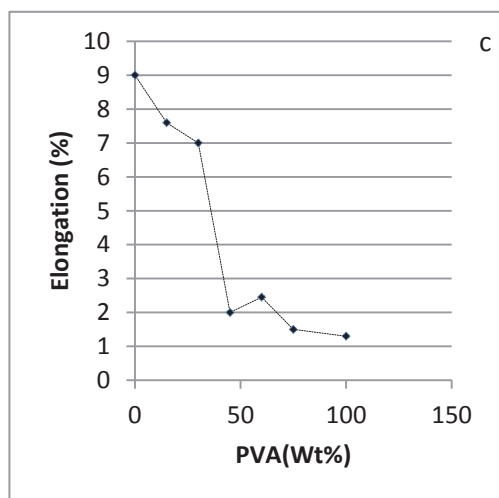
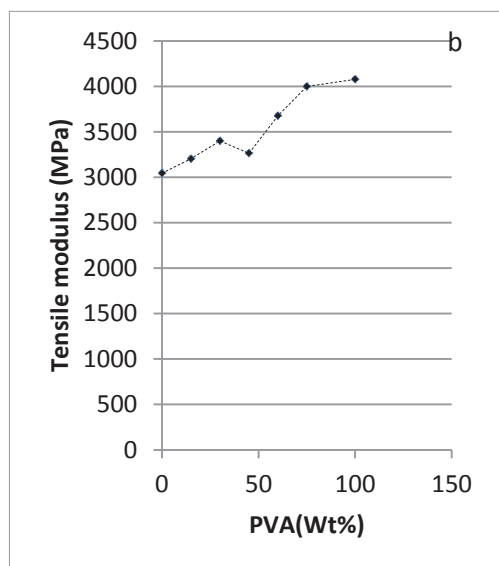
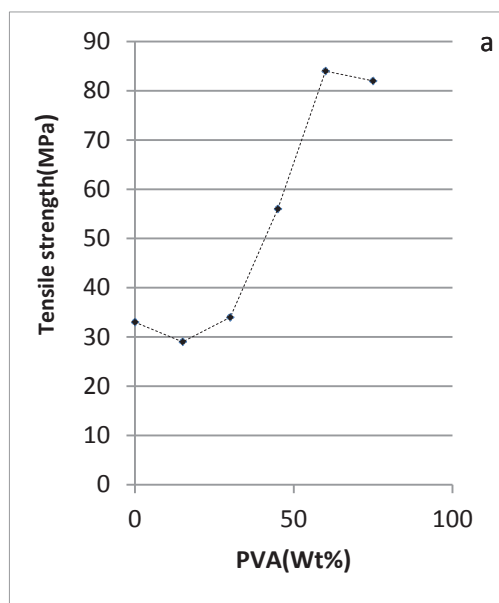


Figure 2: Mechanical Properties for Pullulan/PVA Blend Film in (a) Tensile Strength, (b) and (c) Elongation (%).

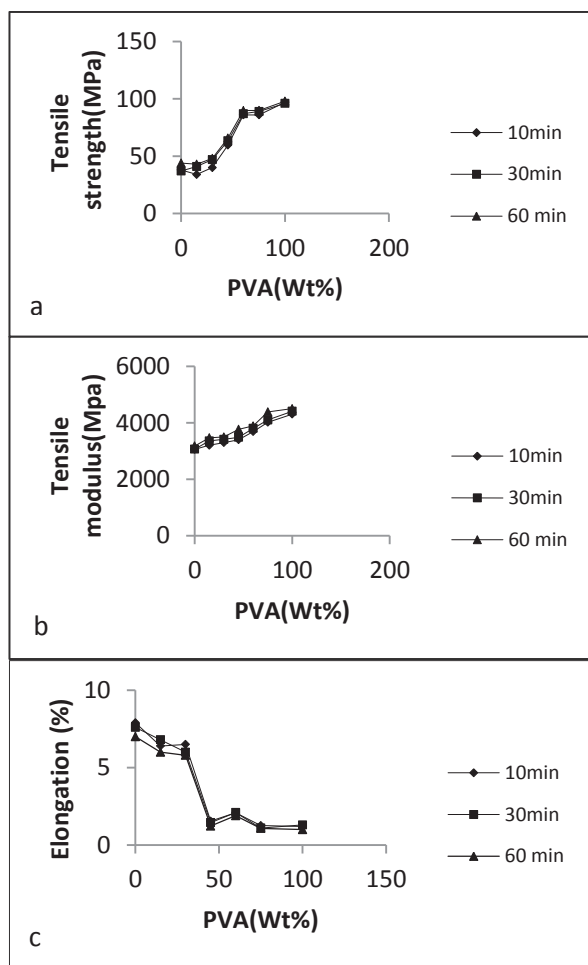


Figure 3: Mechanical Properties for Pullulan/PVA Blend Film cross linked with (GA) at 10, 30 and 60 min in (a) Tensile Strength, (b) Tensile Modulus and (c) Elongation (%).

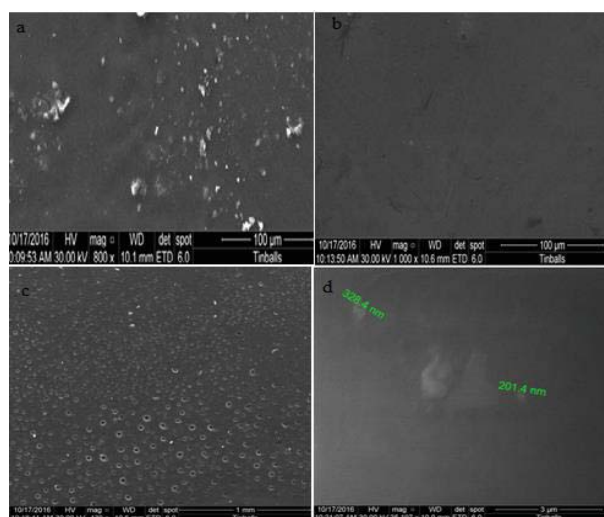


Figure 4: Scanning Electron Microscopy (SEM) of Pure Pullulan Film (a), Pure PVA film (b), Pullulan /PVA (c) and Cross-Linked Pullulan /PVA.

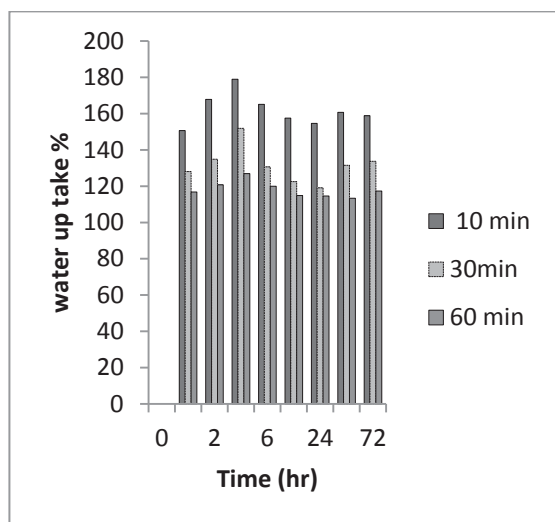
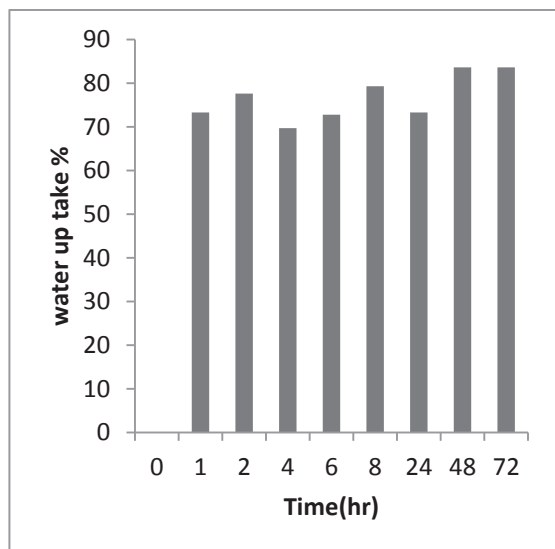


Figure 5: water up take behavior of PVA/Pullulan in (a) and cross-linked PVA /Pullulan film at different time of cross linking reaction.

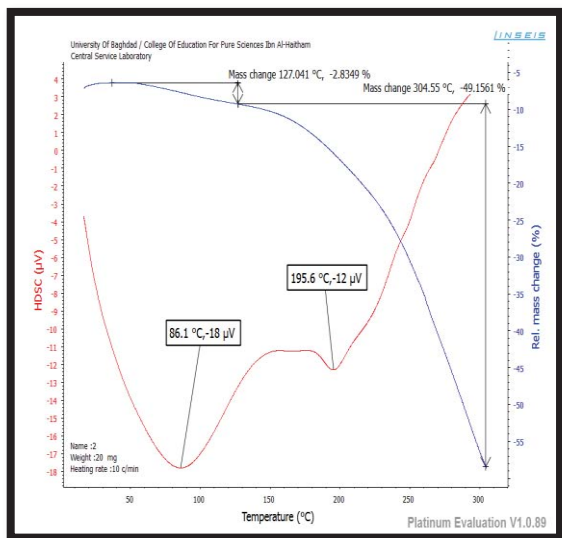


Figure: 6 DSC and TGA for the Pull/PVA.

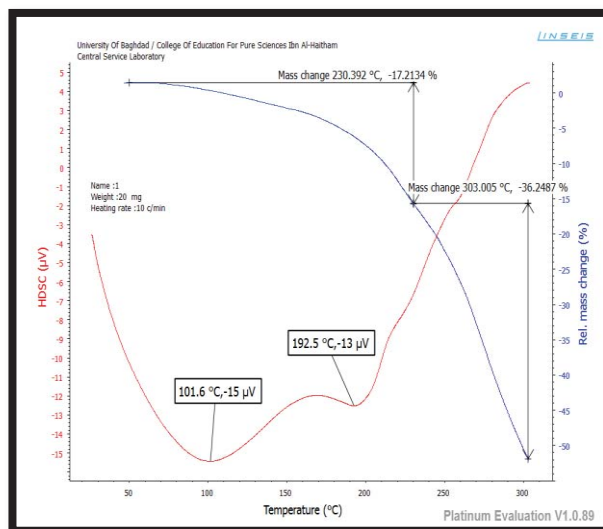


Figure 7: DSC and TGA for the pull/PVA cross linked with GA.

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