

The use of pectin to synthesis and characterize hydrogel (composite, grafting and blending) and study of some water retention properties

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Article Information	Abstract
<p>Received: 01/09/2020 Accepted: 18/10/2020</p>	<p>This research was conducted to purpose preparing and characterization various types of hydrogels such as blending, composite and grafting. This was done by reacting monomers such as acrylamide (A.M), methyl acrylate (M.A) and polymers. Polyvinyl Pyrrolidone (PVP) and carboxymethyl cellulose (CMC) with pectin was prepared from citrus peels. Hydrogel polymers (graft, blend and composite) were characterized using different techniques such as Fourier Transformed Infrared spectroscopy (FT-IR), Differential Scanning Calorimetry (DSC) and Scanning Electron Microscopy (SEM). The results of the reactions were identical to the theoretical expectations. The study was conducted to find out some properties such as swelling in water and absorption at different temperatures 25 °C and 20 °C, and the results were shown as a (559.9%, 429.2%) and (515.2%, 363.2%) respectively.</p>
<p>Keywords:</p> <p><i>Swelling, Hydrogel, Grafting hydrogel, Pectin, Composite hydrogel.</i></p>	

Introduction:

Hydrogels are polymeric nets have the ability to absorb large quantities of water [1]. Hydrogel is a hydrophilic material. Swell in water instead of dissolving in it. The reason is that they are hydrophilic because they are intertwined and the presence of polar groups in their chemical composition, which lead to the formation of hydrogen bonds with water molecules [2]. The hydrogels swell in the water but do not dissolve due to the three-dimensional shape of the hydrophilic cross-linked polymer [3]. Hydrogel has a different classifications, for instance, it can be classified according to the source such as (natural, prepared) and, hybrid, as well as it was classified according to the type of preparation such as copolymer, homo-polymer and Interpenetrating also it can be classified according to crosslink such as physical hydrogel and chemical hydrogel [4-6].

Pectin is a polysaccharide, which is a heterogeneous polymer, containing large quantities of (D-galacturonic acid) cross-linked by α - (1-4) groups, and that the ester is an analogue in the form of carboxyl groups. Pectin can be divided by the degree of esterification DE, where pectin is said to be high methoxyl when DE is more than 50% [7]. Pectin is a substance that is added to food as an emulsifier and thickener [8]. Pectin was extracted by ultrasound in previous studies and extracted by hot water and acid such as citric and nitric [9,10]. Pectin extracted from citrus peels is used as feed for livestock [11]. Pectin-based biomaterials are

used for wound dressing, tissue engineering, and drug delivery [12]. Pectin resists the stomach and other intestinal enzymes such as amylase in the upper digestive system and the protease. Also, the digestion of pectinases resulting from coliform bacteria is easy, and this feature makes pectin a medium that works to deliver the drug to the colon [13]. Pectin is also used to lower blood cholesterol, inhibit lipase activity and heal wounds, as pectin is the main component of citrus fruits [14].

The polyvinyl pyrrolidone PVP is widely used in biomedicine because it is biodegradable and is one of the synthetic polymers and is biocompatible which can form hydrogels through physical or chemical crosslinking [15]. Carboxymethyl cellulose CMC is a naturally occurring cellulose-derived, water-soluble, hydrophilic and non-toxic polymer that is widely used in oil and detergent exploration and the food, paper and textile industries due to its viscosity [16].

Materials and Methods

Instrumental:

Infra-Red spectral (FT-IR) cm^{-1} (SHIMADZU), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM), Sensitive Balance (sartorius/ AG Gottingen) (Germany), Oven (Fanem/ Orion 520 Sao Paulo-Brasil), Hot Plate (Electro Thermocline) (England), Mechanical stirrer (Qallenhamp England).

Materials:

Methyl acrylate (M.A) (Sigma-Aldrich), Ammonium persulfate (APS), (Hopkin and Williams), citrus Peels, Chloroacetic acid (BDH, England), Sodium hydroxide (BDH), Ethanol (absolute) (British Drug Houses BDH 95%), N, N-dimethyl-bis-acrylamide MBA (Sigma-Aldrich), polyvinyl pyrrolidone PVP (Sigma-Aldrich).

Blend hydrogel preparation.

Preparation of Pectin/PVP blends hydrogel.

This type of hydrogel is prepared using an MBA, as the following:

The solution of pectin is prepared by adding (1g) of pectin to 15 mL of distilled water and stirred using a Magnetic Stirrer for 1 hour until a homogeneous solution is formed.

Another solution of PVP is prepared by adding (1g) of PVP to the 15 mL distilled water and stirring for 1 hour until it is completely dissolved and a homogeneous solution is formed. The solution is prepared at a temperature of 60°C along the stirring process. Then the two solutions (pectin and PVP) are mixed and stirred at the same degree for 10 minutes time. Then 0.04 g of MBA was dissolved in 5 mL of distilled water and added as a cross-linked to the reaction mixture. Stirring continues for (8hrs) until a highly absorbent mixed hydrogel is formed and it left at room temperature for approximately 6 days until dry.

Preparation of grafting hydrogel

Preparation of Pectin-g-MA hydrogel [17]

17 mL of 0.5% NaOH was added in a three-necked reactor with (1g) of pectin and the mixture was stirred for 15 minutes using the magnetic stirrer. 16 mL of Chloroacetic acid was added to the reaction and stirrer for 20 minutes at 60°C . After that the reaction was transferred to the water bath and stirred for 5 minutes by using a Mechanical stirred under nitrogen gas. 0.7 g of APS (dissolved in 5 mL of distilled water) was added to the reaction and stirred for 15 minutes. Then add 2 mL of M.A and after 15 minutes was added 0.05 g of MBA

(dissolved in 5 ml of distilled water). The mixture was stirred for three hours in the water bath at 80°C. The product was cooled at room temperature and was immersed in 40 mL of ethanol for a 1 day. Then it filtered and dried at (75-80) °C for several hours until it completely dries.

Preparation of grafting composite hydrogel.

CMC-g-poly (acrylamide)/pectin composite superabsorbent hydrogels [18]

This type of superabsorbent hydrogel is prepared by dissolving 0.67 g of CMC in 36 mL of distilled water, in three-necked round bottom flask. The solution was stirred at 80 °C with a mechanical stirrer until the CMC is completely dissolved. After that, 0.26 g of pectin (dissolved in 5ml of distilled water) was added to the reaction with stirring for 20 minutes. Then add 2 mL of A.M to the reaction and 0.04g MBA (dissolved in 5ml of water) was also added to the reaction with stirring for 15 minutes. After that 0.6g of APS (dissolved in 5 mL of distilled water) was added to the reaction. Stirring continues until the hydrogel was formed, then the product was left to cool to room temperature, and then add to the mixture 30 mL of ethanol for 3hrs, where a gel layer was observed to be white colour. After that, the ethanol is replaced with 55 mL ethanol again and left for 1 week then the product was filtered and dried at 50 °C for 1 week until it dries completely.

Swelling of hydrogel.

Water absorption was measured by the prepared hydrogel by weighing a quantity of hydrogel that is completely dry. After that, put it in 100 mL of distilled water, using two temperatures 20°C and 25 °C for 24hrs. Then the weight is measured again after the hydration process. Then calculate the percentage of the amount of water absorbed by calculating the change in weight before and after hydration as follows:

$$Q = \frac{w' - w}{w} \times 100\%$$

Q: The percentage of Absorption amount.

W': Weight of Hydrogel after Hydration.

W: Weigh the Hydrogel before Moisturizing.

Characterization of the Hydrogel.

The hydrogel was characterized using scanning electron microscope (SEM), Fourier transform infrared (FTIR) with the range from (400-4000) cm⁻¹, and differential scanning calorimetry (DSC) with N₂ gas and heating speed 20 °C /Min.

Samples were sent to Iran for DSC and SEM measurements, as for FT-IR measurements, samples were sent to Baghdad.

Results and Discussion.

To prepare the hydrogel from pectin several experiments were conducted such as blending, grafting and composite hydrogel. Pectin maxed with (PVP, M.A, A.M, and CMC) the results were studied using a set of (SEM, FT-IR and DSC) devices.

FT-IR Spectrum.

Used FT-IR spectroscopy to characterize the hydrogel that prepared from pectin and another material, the hydrogel which characterizing are Pectin/PVP blend hydrogel, Pectin-g-M.A hydrogel and CMC-g-A.M/Pectin composite hydrogel, as shown in Fig. 1.

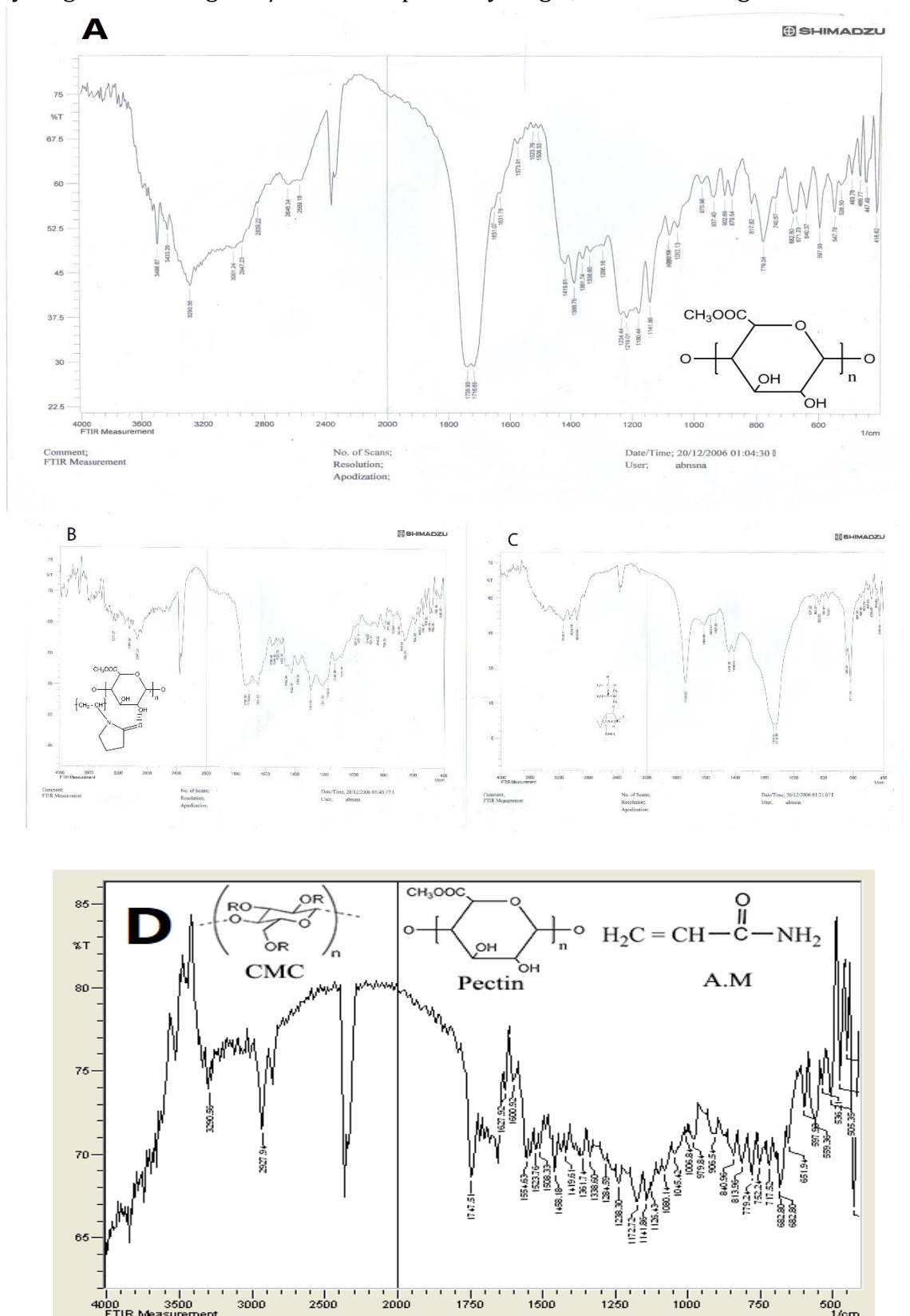


Fig.1 (A): FT-IR spectrum of Pectin, (B): FT-IR spectrum of Pectin / PVP Blend hydrogel, (C): FT-IR spectrum of pectin-g-M. A Hydrogel, (D): FT-IR Spectrum of CMC-g-A.M/Pectin composite hydrogel.

In figure 1 (A) FT-IR spectrum of pectin the (O-H) stretching group located at broad band (3498.87) cm^{-1} , the (C-H) stretching group located at peak (2947.23) cm^{-1} , (C=O) group located at the peak (1735.93) cm^{-1} . In figure (1) (B) FT-IR of pectin/PVP hydrogel the (O-H) stretching, (C-H) stretching and (C=O) groups appears at the located at (3271.27) cm^{-1} , (2947.23) cm^{-1} and (1735.93) cm^{-1} respectively. In the figure (1) (C) groups (OH) stretching, (C-H) stretching, and (C=O) appears at located (3140.11), (2954.93), (1735.93) cm^{-1} respectively for FT-IR spectrum of Pectin-g-M.A. In the same figure (D) FT-IR for the hydrogel CMC-g-A.M /pectin the groups (O-H), (C-H) and (C=O) appears at located (3290.65) cm^{-1} , (2937.94) cm^{-1} and (1747.51) cm^{-1} respectively.

Differential Scanning Calorimetry (DSC).

To determine the mixing process of hydrogel polymers used DSC. In figures 2 (A) and (B) DSC of pectin and CMC-g-A.M/ pectin hydrogel. Where it shows several properties, such as glass transition (T_g) and melting temperature (T_m).

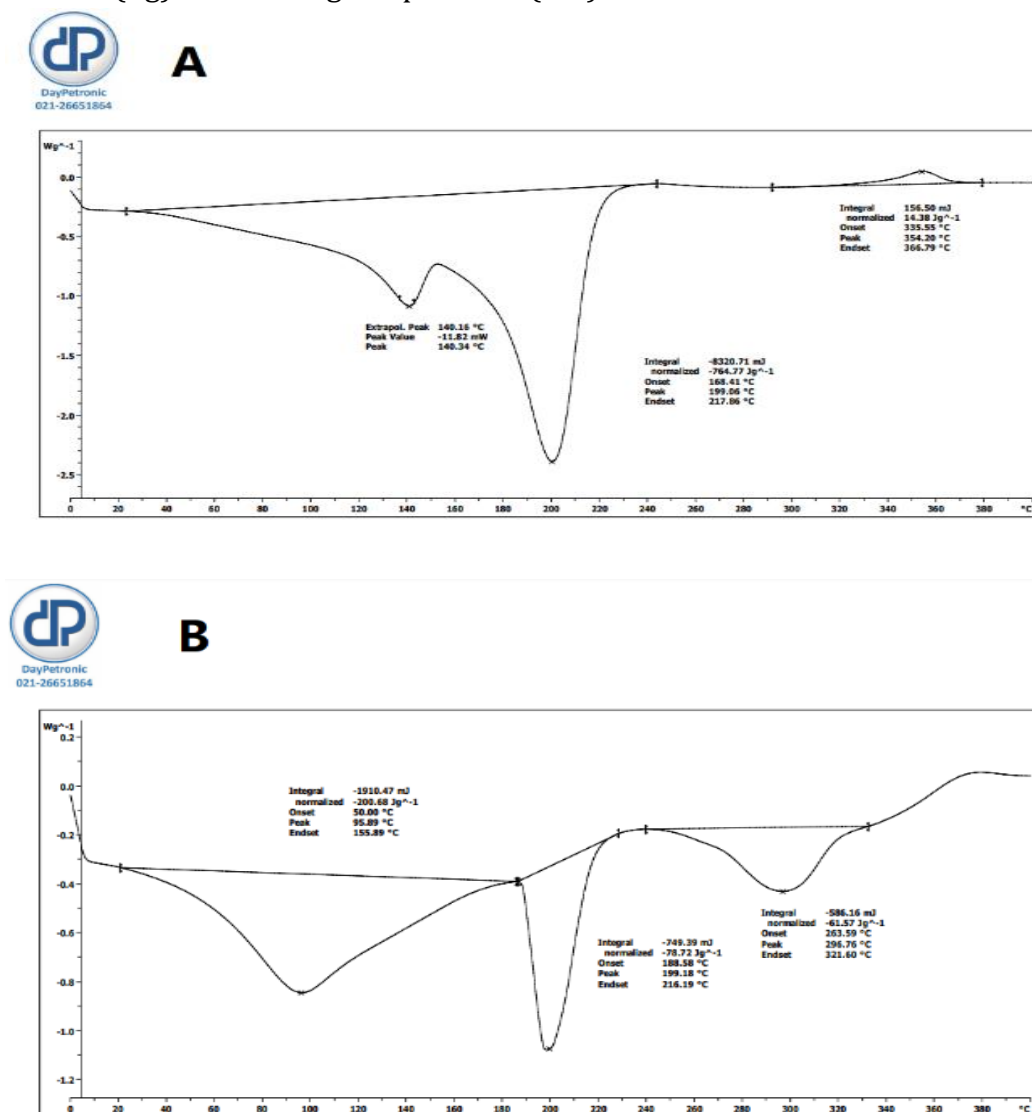


Fig.2 (A) DSC of pectin, (B) DSC of CMC-g-A.M/pectin composite hydrogel.

In figure 2 (A) glass transition (T_g) appear at temperature 68 °C and small endothermic peak appear at temperature 140 °C, the peak can be seen at 199 °C which indicates (T_m). In

figure 2 (B) the value of T_g is 19 °C, the peak at 95 °C for the degree of crystallization, and the peak at 199 °C is T_m and it's the same degree in pectin alone. The rest of temperature as shown in the table 1.

Table 1: The thermal properties of pectin and CMC-g-A.M/pectin hydrogel.

Compounds	Onset temperature °C	Melt End set temperature °C	Melt peak temperature °C
Pectin	168	217	199
	335	366	354
CMC-g-A.M/pectin composite hydrogel	50	155	95
	188	216	199
	263	321	296

Scanning Electron Microscope (SEM).

A SEM of PVP and pectin/ PVP hydrogel showing a surface image for two compounds as show in figure 3.

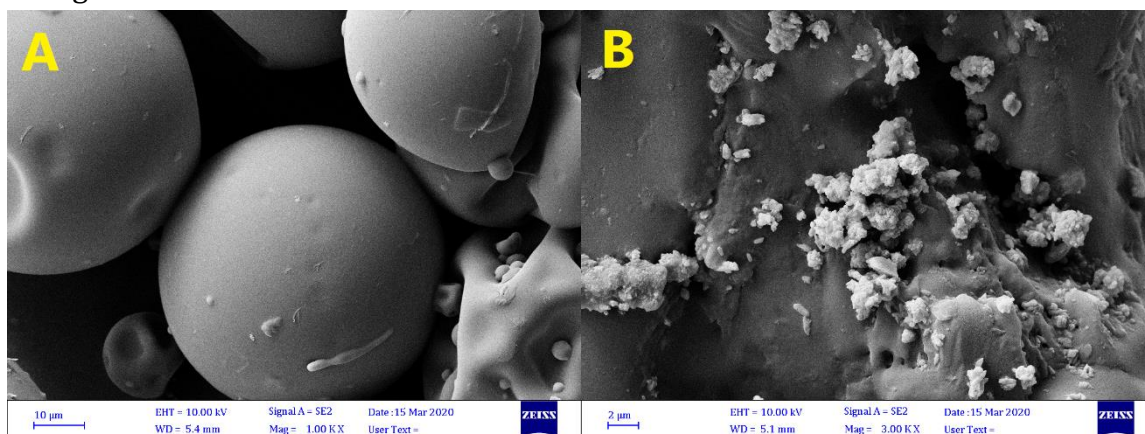


Fig.3 (A) SEM of PVP, (B) SEM of hydrogel pectin/ PVP.

Calculate the absorption amount of the prepared hydrogel.

The absorption was calculated, during the practical part for the prepared hydrogel using temperatures 20 °C and 25 °C and the results were shown table 2 and table 3:

Table 2: The difference in the absorption amount of the hydrogel at 20 °C.

Hydrogel	Wight hydrogel before hydration (g)	Wight of hydrogel after hydration (g)	Absorption percentage
Pectin/PVP	0.2914	1.3499	363.2
Pectin-g-M. A	0.2736	1.5294	458.9
CMC-g-A.M/pectin	0.2762	1.6992	515.2

Table 3: The difference in the absorption amount of the hydrogel at 25 °C.

Hydrogel	Wight hydrogel before hydration (g)	Wight of hydrogel after hydration (g)	Absorption percentage
Pectin/PVP	0.2650	1.4025	429.2
Pectin-g-M.A	0.2156	1.0142	370.4
CMC-g-A.M/pectin	0.2470	1.6301	559.9

In hydrogel the amount of absorption depends on several variables such as polymers and monomers used material of the cross-link, the absorption process is adopted on the polarized groups in the hydrogel and the concentration of the initial.

It was found in table 2 and table 3 that the temperature had a great effect on the hydrogel swelling process. Where when the temperature is low the swelling process is low, As for the case where the temperature rises, the swelling process increases in the hydrogel. This means that the higher the temperature, the more the swelling process will increase. But with the high temperature rise, the hydrogel will lose its properties and give a contradictory result. Where it begins with a rise in swelling and sometimes a decrease in swelling and sometimes leads to a loss of the substance because the substance decomposes [19].

Used APS lead to increase the swelling process as the free radicals will increase and this lead to increased polymerization , the rate of swelling increase when the time increase [20,21]

Conclusion.

It is possible to prepare the hydrogel from pectin that the results of the research showed, which was extracted from fruit peels and agricultural waste. Overlays can be successfully prepared with A.M and blending with PVP and grafting with M.A. Absorption results were high in prepares hydrogel, which meant successful preparation.

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استخدام البكتين لتحضير وتشخيص الهيدروجيل (المتراكب والمطعم والمختلط) ودراسة بعض خصائص احتجاز الماء

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البحث مستل من رسالة ماجستير الباحث الاول

الخلاصة:

معلومات البحث:

تم اجراء هذا البحث لتحضير وتشخيص مختلف الأنواع من الهيدروجيل مثل المختلط والمتراكب والمطعم. اجري هذا بمفاعلة مونومرات مثل الاكريل اميد (AM) والمثيل اكريليت (MA) وبوليمرات مثل بولي فينايل بايروليدين (PVP) و كربوكسي مثيل سيليلوز (CMC) مع البكتين الذي تم تحضيره من قشور الحمضيات. بوليمرات الهيدروجيل (المطعمة والمختلطة والمتراكبة) شخصت باستخدام تقنيات مختلفة مثل مطيافية الأشعة تحت الحمراء (FT-IR) والمسح الحراري التفاضلي (DSC) والمجهر الماسح الالكتروني (SEM). كانت نتائج التفاعلات مطابقة للفرضيات النظرية. بعدها أجريت دراسة لايجاد بعض الخواص مثل الانتفاخ في الماء وعملية الامتصاص و بدرجات الحرارة °C 20 وكانت النتائج (559.9, 429.2) و (515.9, 363.2) على التوالي.

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الكلمات المفتاحية:

عملية الانتفاخ، هيدروجيل، هيدروجيل مطعم، بكتين، هيدروجيل متراكب.