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ORIGINAL PAPER

Grafting of Acrylamide onto Polysaccharides Blend Using Photo-initiators

Marwa M. El-Sayed[1] · Mohamed H. Sorour[1] · Nabil Abd El Moneem[2] · Hayam Shalaan[1] · Sahar El Marsafy[2]

Abstract The present paper comprises of hydrogel synthesis processes using a blend of three natural polysaccharides (PsB) "starch, chitosan and alginate" grafted acrylamide (PsB-g-Am) using ultraviolet (UV) irradiation. The grafting process has been undergo using three different photo-initiators [Dimethoxy-2-phenylacetophenone (DMPA), benzoin methyl ether (BME) and benzophenone (BP)]. Furthermore, different PsB/Am weight ratios have been used. The prepared hydrogel has been characterized using XRD and SEM. Grafting percentage (%G), grafting efficiency (%GE), grafting yield (%GY) also have been compared. Among the three used photo-initiators, DMPA gave the maximum attained values of %G (130 %), %GE (72 %) and %GY (89 %) followed by BME and BP, respectively. Swelling water ratio (SWR) for the grafted hydrogels in distilled water (DW) has been studied. Grafted hydrogel using DMPA photo-initiator gave the maximum SWR of 30 g/g. Am/PsB weight ratio and the used photo-initiator had a direct effect on SWR of the produced hydrogel.

Keywords Polysaccharide · Hydrogel · Photo-initiator · Ultraviolet

Introduction

A photo-initiator is a light-sensitive compound which creates free radicals via converting the absorbed light energy (UV or visible light) into chemical energy [11]. The main advantage of using photo-initiator is the possibility to define exact start and end points of the polymerization process via the duration of the irradiation period. In addition, the rate of (most) photo-initiator decomposition is almost independent of the reaction temperature but depends strongly on the light intensity [8, 12, 15, 18].

Irradiation grafting technique is a well-known method for modifying the properties of polymeric materials [1, 3, 9, 14]. Photo-polymerization is creating initiating sites in a specific area, which has been performed on many different types of polymers. Polymerization can be carried out under a wide range of conditions, allowing variations in the produced polymer structures. The effective penetration onto the polymer can be achieved according to the number and type of reactive functional group, temperature, radiation intensity and the used photo-initiator type and concentration [2, 4, 5]. Simple control procedure, no waste and relatively low operating costs make the irradiation technique a suitable choice for the synthesis of hydrogels [7, 10, 13, 17, 23].

Lee et al. and Mubarak et al. [14, 16] used UV in the presence of benzophenone as a photo-initiator for the grafting of acrylic acid and polyvinyl alcohol onto starch, %G of 120 and 98 % were obtained, respectively. Sofia et al. [20] designed a novel polymeric compound based on photo-initiating systems, the mechanisms involved in the formation of the radical and cationic initiating species and finally their application to photo-polymerization has been discussed.

In this study, the synthesis of PsB-g-Am hydrogel using UV technique has been investigated. Moreover, three

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✉ Marwa M. El-Sayed
eng_marwa06@yahoo.com

[1] Chemical Engineering and Pilot Plant Department, National Research Center, El-Bohouth Street (El-Tahrir Street), Dokki, P.O. Box 12622, Cairo, Egypt

[2] Chemical Engineering Department, Faculty of Engineering, Cairo University, Giza, Egypt

different photo-initiators have been used for the hydrogel synthesis. The grafted products were characterized using XRD, SEM, %G, %GE and %GY.

Materials and Methods

Materials

Corn starch (Sigma-Aldrich, Germany), chitosan medium molecular weight (Sigma Aldrich, Germany), alginic acid sodium salt from brown algae “alginate” (Routh, Germany) and acrylamide (Baker Chemical Co., USA) the basic raw materials used for the hydrogel preparation. methylenebisacrylamide (MBA) (Fluka, Germany) has been used as a crosslinker. Dimethoxy-2-phenylacetophenone (DMPA) (Alpha laboratory reagent), benzoin methyl ether (BME) and benzophenone (BP) (Cole-Parmer, India) have been used as photo-initiators. Other chemicals include: acetone, acetic acid and ethanol (El Nasr Pharmaceutical Chemicals Co.). All experiments have been performed using distilled water (DW).

Experiments were conducted using: ultraviolet irradiation system comprises of wood box contains six ultraviolet lamps (15 W each) with wavelength 254 nm (produced from El-Gomhoria company for chemical and laboratory accessories, Egypt).

Methods

Preparation of the Polysaccharides Blend (PsB)

PsB has been prepared as mentioned in our previous work with a small modifications (Sorour et al. [21]). Briefly, starch (3 g) was suspended in 70 ml DW and stirred for 30 min at 80 °C. Chitosan (1 g) was dissolved in 70 ml acidified DW containing 1 wt % acetic acid and stirred for 5 h at room temperature. Alginate (1 g) has been dissolved in 70 ml DW and stirred for 4 h at room temperature. The three solutions have been mixed and stirred for 10 min giving the polysaccharides blend (PsB).

Grafting of Acrylamide onto PsB

Five different weights of Am (3,6,9,12 and 15 g), 0.6 g photo-initiator and 1 g Am have been added to the pre-prepared PsB solution then, 0.1 g of MBA was added to each of the prepared PsB mixtures. Then, grafting step has been done either using UV irradiation technique for 60 min. The reaction product has been allowed to cool to room temperature. Finally, the product was filtered, washed twice with fresh ethanol and dried at 70 °C till constant weight was achieved [19].

Determination of Pertinent Calculations

Determination of Grafting Parameters

Different grafting parameters: grafting percentage (%G), grafting efficiency (%GE), percentage and grafting yield (%GY) have been estimated according to the following equations ([19, 22]):

$$\%\mathrm{G} = \frac{W_1 - W_0}{W_0} \times 100$$

$$\%\mathrm{GE} = \frac{W_1 - W_0}{W_2} \times 100$$

$$\%\mathrm{GY} \frac{W1}{W_0 + W_2} \times 100$$

where $W_{1,}$ W_0 and W_2 denote the weight of grafted product, original polymer and monomer, respectively.

Characterization and Analysis

X-ray Diffraction (XRD)

Philips X-ray diffraction equipment PW/1710 with Monochrom TOR, Cu-radiatio at 40 K.V., 35 mA and scanning speed 0.02°/s.

Scanning Electron Microscope (SEM)

SEM model JEOL: JXA-840A electron probe micro-analyzer coupled with energy dispersive analysis by X-ray (EDEX) has been used for SEM analysis. Hydrogel samples were hydrated with de-ionized (DI) or tap water, frozen in liquid nitrogen overnight. Dried samples were coated with 40 nm gold. All samples were gold coated prior to measurement.

Swelling Water Ratio (SWR)

SWR is generally used to describe the swelling behavior of the prepared hydrogel. The dry hydrogel was soaked in DW for 48 h at room temperature. The swollen samples have been allowed to drain using a plastic strainer for 10 min then; it has been weighed. SWR is given by the following equation [21] SWR (g/g) $= \frac{W_s - W_d}{W_d}$ where W_s and W_d represent the weight of the wet and the dry hydrogel, respectively.

Results and Discussion

Characterization of PsB-g-AAm

X-ray Diffraction

XRD patterns for grafted polysaccharides blend (PsB) prepared using the three different photo-initiators (DMPA, BME and BP) are shown in Fig. 1. Hence, the PsB comprises of starch, chitosan and alginate mixture, XRD patterns (A) present the nature of the three raw polysaccharides. There are crystalline areas observed at 2θ equal to 14.67, 16.97°, 19.67°, 21.97° and 23.87° due to starch and chitosan crystallinity and the non-crystalline area are due to the fact that raw alginate has very small crystallinity. For the three grafted PsB hydrogels, XRD patterns (B, C and D) there are increasing crystallinity areas observed at 2θ equal to 18.7, 21.1°, 23.4°, 28.3°, 38.7°, 43.5° and 48.7° which support the presence of Am in the grafted hydrogel.

SEM

SEM for grafted PsB prepared using the three different photo-initiators are shown in Fig. 2 is another way to proof the occurrence of Am in the PsB. Starch has irregularly oval shape with a smooth surface according to the raw starch nature, chitosan has a flaky nature with irregular shape and porous surface and alginate has a spherical in shape with a relatively smooth surface. For grafted PsB hydrogel prepared using the three different photo-initiators, a clearly different surface morphology is noticed due to the absence either of oval shaped particles or the spherical and presence of a broad network structure and more pores,

Grafting Parameters for PsB Using Different Initiators

For UV irradiation technique, three different photo-initiators [Dimethoxy-2-phenylacetophenone (DMPA), benzoin methyl ether (BME) and benzophenone (BP)] have been studied at different Am/PsB weight ratios.

Grafting Percentage

Figure 3 represents grafting percentage for PsB-g-Am prepared using three different photo-initiators. The maximum attained %G was 130 % using DMPA photo-initiator followed by 124 and 118 % for BME and BP, respectively at the maximum Am/PsB weight ratio (0.96). It is can be noted that, a slight increase in %G exists with increasing Am/PsB weight ratio (0.6–0.96).

Grafting Efficiency

Figure 4 represents %GE for PsB-g-Am prepared using three different initiators. The maximum attained %GE were 72, 68 and 63 % for DMPA, BME and BP, respectively.

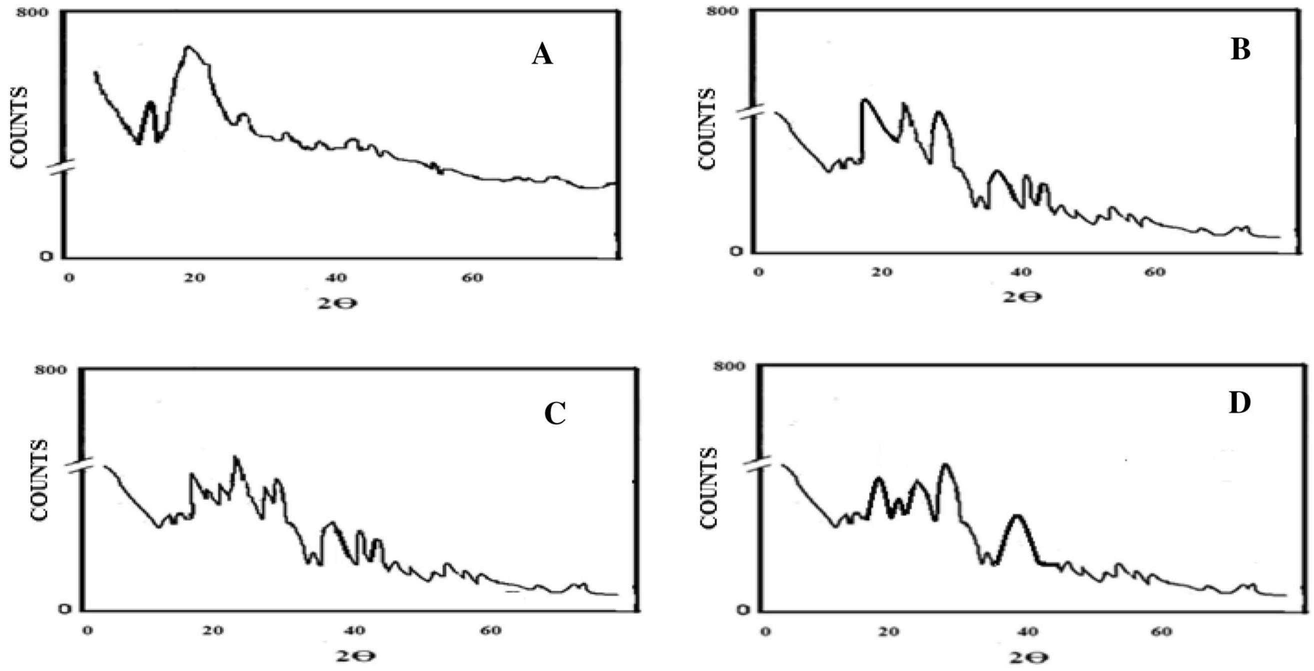


Fig. 1 XRD for PsB (**a**), raw PsB, PsB-g-Am using DMPA (**b**), BME (**c**) and BP (**d**) photo-initiators

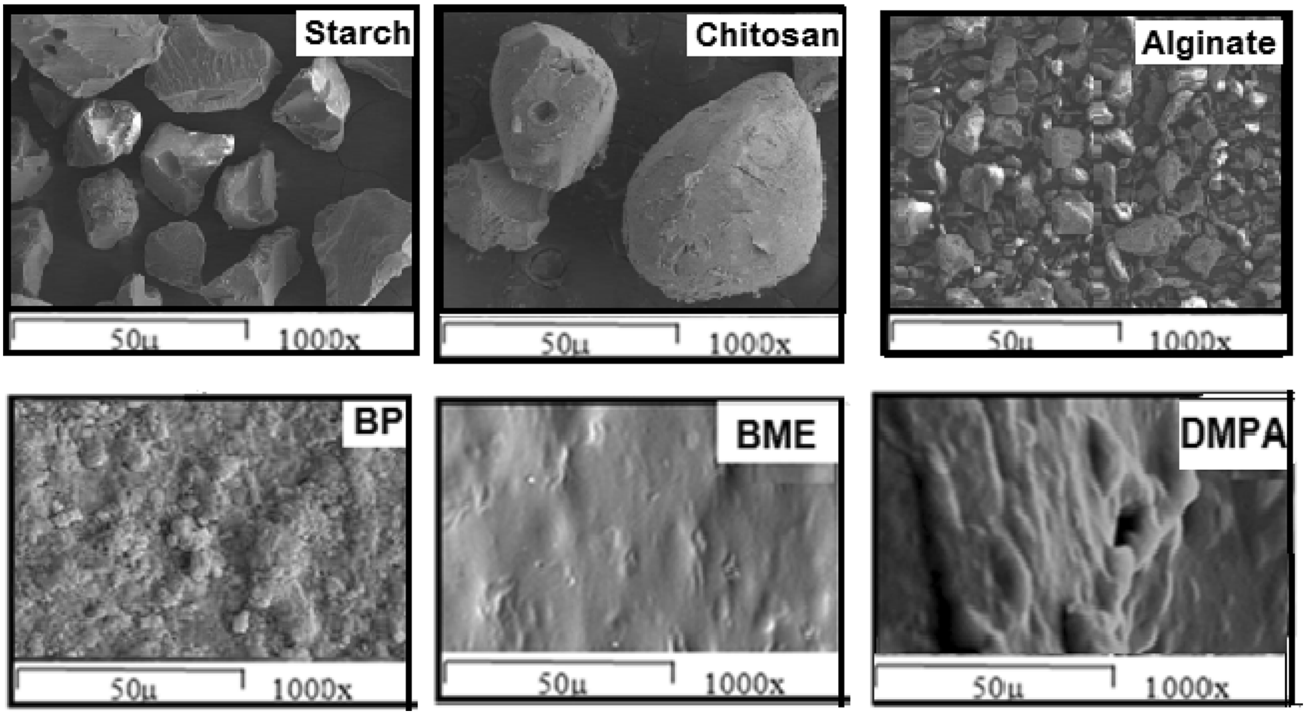


Fig. 2 SEM for the three used polysaccharides starch, chitosan, alginate and for PsB-g-Am hydrogel synthesized using BP, BME and DMPA photo-initiators

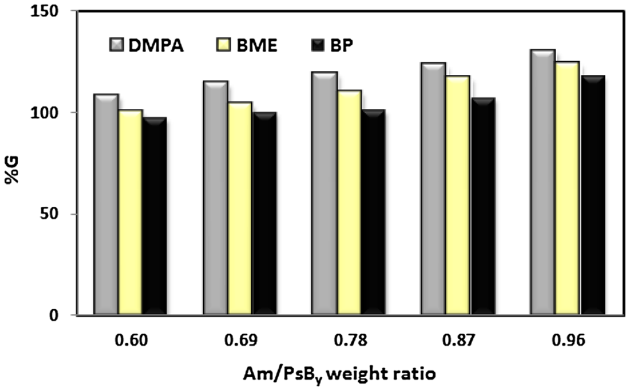


Fig. 3 Grafting percentage for grafting of Am onto PsB using three photo-initiators and different Am/PsB weight ratios

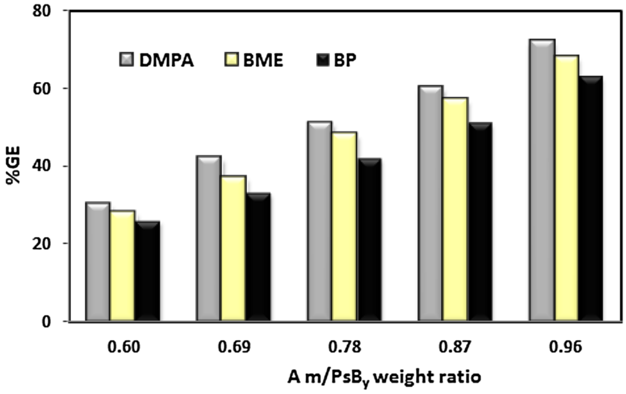


Fig. 4 Grafting efficiency for grafting of Am onto PsB using three photo-initiators and different Am/PsB weight ratios

Grafting Yield

Figure 5 represents %GY for PsB-g-Am prepared using three different photo-initiators. 89, 81 and 79 % were attained using DMPA, BMA and BP, respectively.

SWR in DW

SWR in DW after 48 h has been studied for the grafted hydrogel prepared using three photo-initiators as shown in Figs. 6, 7 and 8. It was noticed that, for all the used photo-initiators SWR was increased with increasing Am/PsB weight ratio and maximum SWR was 30, 22 and 20 g/g using Am/PsB of 0.96 for DMPA, BME and BP, respectively. Initial increasing in SWR was originated from the greater availability of monomer molecules in the vicinity of the chain propagating sites of PsB macro-radicals and higher Am content enhances the hydrophilicity of the hydrogel in PsB-g-PAm that, in turn, causes a stronger affinity for more absorption of water. This phenomena is probably due to: (1) preferential homo-polymerization over graft copolymerization (2) an increase in the viscosity of the medium, which hinders the movement of free radicals

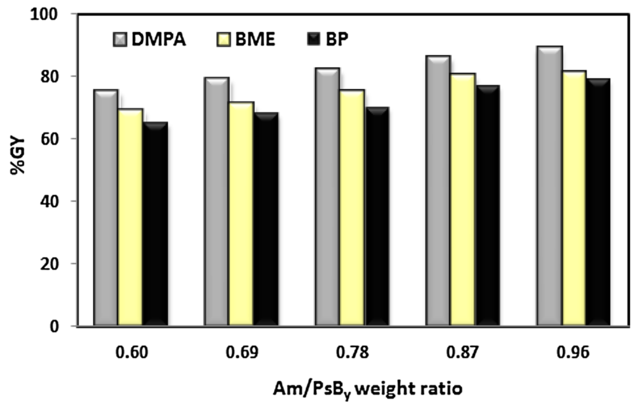


Fig. 5 Grafting yield for grafting of Am onto PsB using three photoinitiators and different Am/PsB weight ratios

and monomer molecules, and (3) the enhanced chance of chain transfer to monomer molecules [6].

Conclusion

This paper has discussed the use of the photo-initiator in the photo-polymerization area. It also gave the opportunity to recall some interesting data PsB comprising starch, chitosan, and alginate blend has been grafted with acrylamide using three different photo-initiators. Five Am/PsB weight ratios have been used. SEM and XRD have been used to approve the occurrence of acrylamide into the polymer chain using the UV technique. It is noticed that

Fig. 6 SWR for PsB-g-Am using PB photo-initiator using different PsB/Am weight ratios

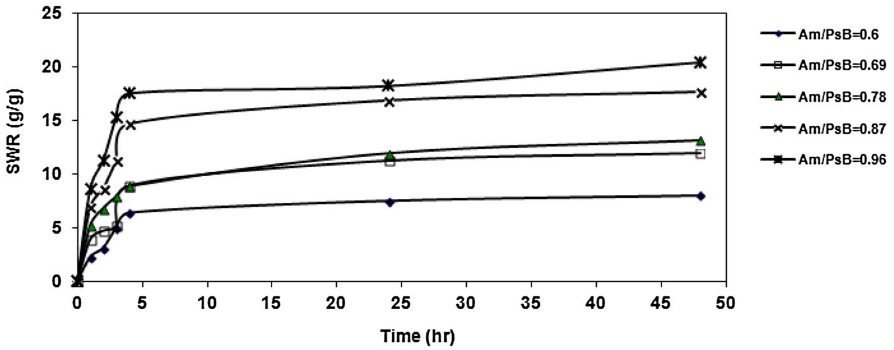


Fig. 7 SWR for PsB-g-Am using DME photo-initiator using different PsB/Am weight ratios

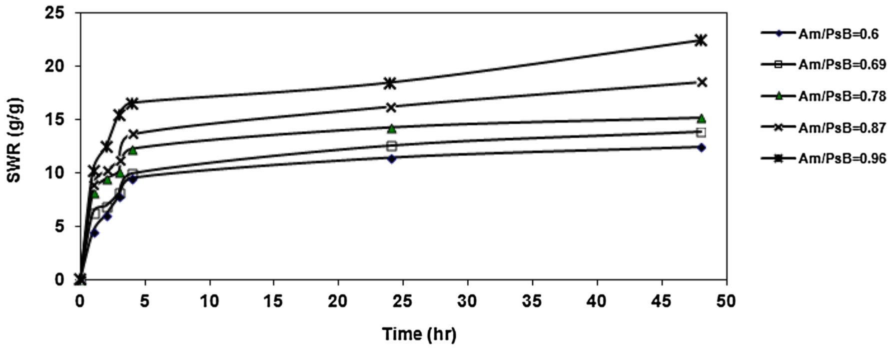
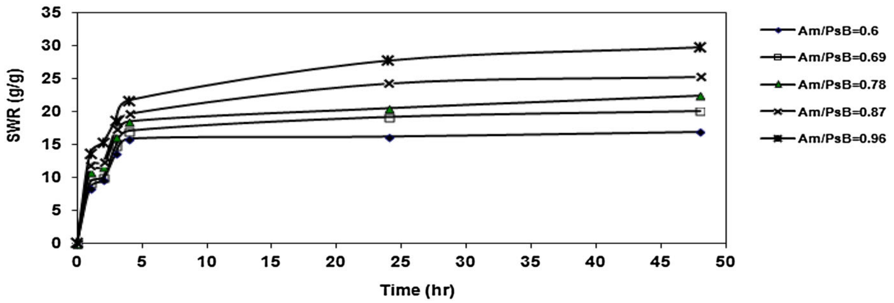


Fig. 8 SWR for PsB-g-Am using DMPA photo-initiator using different PsB/Am weight ratios



changing the photo-initiator type has a slit effect in the different grafting parameters. Swelling water ratio of the synthesized hydrogel has been studied. SWR in DW was ranging from 2 to 30 g/g using different Am/PsB weight ratios and photo-initiators. The maximum attained values of %G, %GE, and %GY for UV prepared hydrogel were 130, 72, and 89 %, respectively for Am/PsB weight ratio of 0.96.

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