



Preparation and Characterization of Polymer Blends Based on Carboxymethyl Cellulose, Polyvinyl Alcohol, and Polyvinylpyrrolidone



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Abstract

Two libraries of crosslinked polymer blends were synthesized and characterized. The polymer blends were prepared from carboxymethyl cellulose, polyvinyl alcohol, and polyvinylpyrrolidone in 1:1:1 ratio using solvent casting method. Two crosslinking agents were used: glyoxal and glutaraldehyde for the first and second libraries respectively. Both crosslinking agents were used in three different ratios (10, 15, and 20%). The mechanical properties of the polymer blends were tested using morphology, and swelling ratio methods for the crosslinked polymer blends only. The results confirm that the degree of crystallinity was altered during blending and crosslinking when the original polymer blend compared to itself after crosslinking. The maximum elongation $\epsilon_{M\%}$ was found when the crosslinking agent ratio was 15%. The polymer blend **D** with glutaraldehyde as the crosslinking agent had the maximum elongation $\epsilon_{M\%} = 17.533$, and about 0.565 Mpa Young modulus. While polymer blend **B** with glyoxal as crosslinking agent had maximum elongation $\epsilon_{M\%} = 11.115$, and about 0.593 Mpa Young modulus. Finally, the prepared blends are suitable for adsorption and as an excipient material in pharmaceutical industries.

Keywords: crosslinking agents; mechanical properties; PVP; PVA; and CMC.

1. Introduction

Biodegradable polymers have great attention due to their wide range of applications in pharmaceutical, nutritional, and biomedical fields.¹ These polymers are derived from natural, semisynthetic, or synthetic sources. Semi-synthetic biodegradable polymers such as carboxymethylcellulose (CMC) (figure 1-a) is one of the most used safe polymers in food, laundry detergents, and soil.² It is derived from cellulose with carboxymethyl (-CH₂COOH) group bonded to some of the hydroxyl groups in the cellulose.³ Cellulose is the most abundant biopolymer in nature, and it can be supplied from plants in large quantities.⁴

The artificial polymers such as Polyvinyl alcohol (PVA) (figure 1-b) and Polyvinylpyrrolidone (PVP) (figure 1-c) are synthesized from petroleum sources mainly.⁵ PVA is used in food packaging, paper

industry, and textile. PVP is extensively used in pharmacy and medicine.⁶

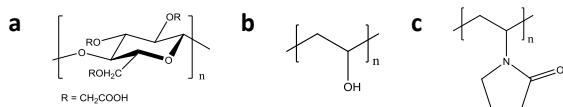


Figure 1: Structures of: carboxymethylcellulose (CMC) (a), Polyvinyl alcohol (PVA) (b), Polyvinylpyrrolidone (PVP).

Crosslinking agents are chemical compounds with two or more functional groups that are connecting polymer sidechains through chemical bonds to form a three-dimensional network. These cross-linking agents such as aldehyde, carboxylic, and silica derivatives were used in biodegradable polymers because they had low toxicity hazards and can interact efficiently with cellulose rendering products with unique properties.⁷⁻¹⁰ Dialdehydes such as

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glutaraldehyde and glyoxal are one of most valuable crosslinking agents.

Glutaraldehyde is one of the most used crosslinking agents because it is a very efficient, inexpensive, and commercially available.¹¹ It is used in microscopy, leather tanning, and enzyme technology. Glutaraldehyde is used mostly with polymers that have amino residues to form imine bonds.¹²⁻¹⁵

Glyoxal can be obtained from natural resources.¹⁶ It is a widely used papermaking industry and in biodegradable films.¹⁷ Glyoxal is non-toxic, biodegradable, and inexpensive.¹⁸ It is approved to be used in food up to 6% by the Food and Drug Administration (FDA).¹⁹

Plasticizers are low vapor pressure, low molecular weight, and inert molecules. These molecules are used mainly to improve polymer flexibility.²⁰ Sorbitol is one of the best-used plasticizers. It is FDA approved to be used as a food additive.¹⁹ Sorbitol is acting as a plasticizer by forming hydrogen bonds. It is relatively thermal stable.

Polysaccharides and polyvinyl alcohol mixtures can be used in combination for an assortment of applications where one of the polymers will promote the properties of the other polymer. Research on these mixtures has been very essential so far, scout the different possibilities of the optimizer and make better the properties of the very discordant polymers.

There has been a significant interest in biomaterials over the past decades. Many types of polymeric blends have been prepared and studied for applications such as food preservatives and medical delivery materials recently.²¹ Natural hydrogels such as PVP/CMC, dextran/polyacrylic acid, starch/PVA²² ref chitosan/PVA²³, chitosan/poly(ethylene oxide) have inherent physical-chemical and biological properties, as well as many biomedical applications (for example, wound healing, drug delivery, and treatment of nerve tissue).²⁴⁻²⁸

In this study, three proportions of the cross-linking agents (10, 15, and 20%) were utilized to obtain the best mechanical properties or swelling in water. We examine the preparation of PVP/CMC-based hydrogel and its characterization of mechanical properties, swelling ratio in a water medium, and the morphology of the prepared polymer blends. A chain of PVP/CMC/PVA polymer blends hydrogels were prepared with a stable PVP/CMC/PVA ratio with different ratios of crosslinking agents to fulfill the efficient content of the composition.

2. Experimental

PVP K 30 (PVP: molecular weight 40,000), (PVA: average molecular weight 3015-3685), were supplied by Fluka, Switzerland; carboxymethyl cellulose (CMC: preswollen, micro granular) Glutaraldehyde (25% in H₂O, Grade 1), Glyoxal and HCl (35–38%)

were purchased from Sigma -Aldrich, USA; sorbitol was obtained from Lachema, Czech Republic.

2.1. Preparation of polymer blends

PVA, PVP, and CMC were blended at a (1:1:1) w/w ratio. An equal weight of PVP, PVA, and CMC in an aqueous solution was mixed at 40 °C in the presence of 20% of sorbitol as a plasticizing agent. The mixture was stirred for 4 hours using mechanical stirrer. Then three different weight ratios of glyoxal (10, 15, and 20) w/w% were added in presence of HCl to make three different crosslinked polymers. The mixture was stirred for 30 minutes and the product was poured at Petri dishes to form hydrogel film. The films were dried at room temperature for 24h. Same method was applied to prepare the second polymer library with Glutaraldehyde as the crosslinking agent. The compositions of each component in the crosslinked polymer blends are shown in Table (1).

Table 1: The components in the hydrogel polymer blends.

Symbol	Glyoxal %	Glutaraldehyde%	PVP/PVA/CMC
A	10	0	1:1:1
B	15	0	1:1:1
C	20	0	1:1:1
D	0	10	1:1:1
E	0	15	1:1:1
F	0	20	1:1:1

3. Testing methods

3.1 Mechanical Properties

Young Modulus (E), maximum elongation (ϵ_m), and elongation at break (ϵ_B) were tested on 3 specimens for every sample. Rectangular test specimens with a length of 100 mm, a width of (10 mm), and a thickness of about 200 μm were used as specified in ISO 527-3. The analysis was carried out at room temperature using a universal testing machine Zwick Rell was used, this device's origin Germany, from type BTI-FR 2.5TN.D14, power operating card 100-129 V / 4,4-3,7). Sorbitol-based polymer blends of CMC/PVA/PVP were prepared by simply introducing sorbitol as a plasticizer and two kinds of crosslinking agents amended the tensile properties over commonplace every polymer alone.

3.2 FESEM Scanning Electron Microscopy

Scanning electron microscopy (SEM) trial was carried out on FESEM =FEI NOVA NANOSEM 4501 running in the high vacuum/ secondary electron imaging mode at a quicken voltage of 5-20 kV. The samples of polymer blends were coated with a thin layer of an alloy of a palladium/gold to progress the

surface conductivity and tilted 35° for better monitorization. The photos were taken at a magnification of 3 x1000k x and 6 x1000kx. SEM is a highly useful method for visual substantiation of surface morphology and the physical state of the compound surfaces.

3.3 Study of Swelling Behavior

For the water absorption, prorated swelling is calculated from the difference between a dry sample and wet sample weights of the specimens divided by the dry weight. This was calculated after immersion of the polymer blend disks specimens in water. The immersed polymer blend discs were removed, gently wiped with a soft tissue to take off water from the surface of the disks, and then the weight was measured. The procedure was repeated until reach to the stable weight according to the following equation:^{25, 29}

the grade of swelling was studied where, W_s and W_d symbolize the weight of swollen polymer blend disks and dry one, respectively. When a polymer swells due to water absorption, the length of the diffusion pathways increases. Once a water tenor specific to each polymer is reached, the polymer's ability to get about steeply increases in a phenomenon called "polymer chain relaxation" or "glassy-to-rubbery phase transition. The swelling behaviour of the hydrogels was measured in distilled water to assess the extent of their water uptake ability. Huge water retention extent is one of the main characteristics of hydrogels.

4. Results and discussion

4.1 Mechanical properties

Figures 2 and 3 show the stress-strain curves on polymer libraries (**A**, **B**, and **C**) and (**D**, **E**, and **F**) respectively. The force for (**A**, **B**, and **C**) was in the following order **A**>**B**>**C** with **A** sample force around 50N

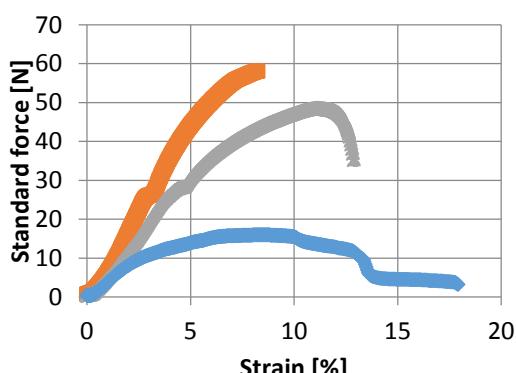


Figure 2: Stress-strain curves of the A, B, and C polymer blends

While the seconds library had the following order **E>F>D** with E sample force around 63N.

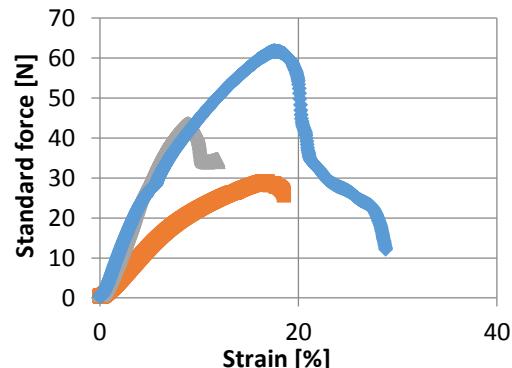


Figure 3: Stress-strain curves of the D, E, and F polymer blends.

Figures 4 and 5 show the relationship between elongation and the percent of the crosslinking agents for both first (**A**, **B**, and **C**) and second (**D**, **E**, and **F**) libraries. Samples **E** and **B** which had moderate percentage of the crosslinking agents (15%) scored the highest elongation (17.533% and 11.115%) respectively. The elongation is affected by type and ratio of the crosslinking agent. A crosslinking agent with ionic and/or hydrogen bonds means more rigid polymer and as a result less elongated. Also, increasing crosslinking agent ratio means less movement for the polymer chains which will lead to less elongation. However, small amounts of the crosslinking will not help to achieve the complete crosslinking between the polymer sidechains. In sample **E**, glutaraldehyde was used as crosslinking agent in comparison to glyoxal in sample **B**. Glutaraldehyde is more flexible than glyoxal because it has 5 carbon chain rather than two in the case of glyoxal.

Mechanical properties of the polymer blends **A-F**: σ_Y (yield strength), σ_M (maximum strength), σ_m (maximum strength), ε_M (maximum elongation), and ε_B (elongation at break) are shown in table 2. Sample E scored the highest maximum strength $\sigma_M = 9.881$ MPa, maximum elongation $\varepsilon_m = 17.533\%$, and elongation at break $\varepsilon_B = 28.775\%$. This makes sample E the best suitable for further testing to be used as flexible wound dressing materials and many similar applications.

4.2.FESEM Micrographs of the Polymer Blends

Morphology and geometry of the dried samples of polymer blends were tested using a scanning electron microscope (SEM) at two different amplification

powers (3000x and 6000x). Figures 6 and 7 indicate the (FESEM) micrographs of the examining polymer blends **B** and **E** respectively. The images reveal the examining polymer blends **B** and **E** respectively. The images reveal the homogeneity of the components in PVP/CMC/PVA hydrogel blends. However, the surfaces of the polymer blend films had bumpy phases. These phases were formed maybe because of the three-equal weight percentage of the polymer mold. However, the fillers tend to form agglomerates at higher loading. It is well known that better dispersion of the plasticizer and crosslinking agent in the matrix is considered as the main factor to achieve good mechanical properties.

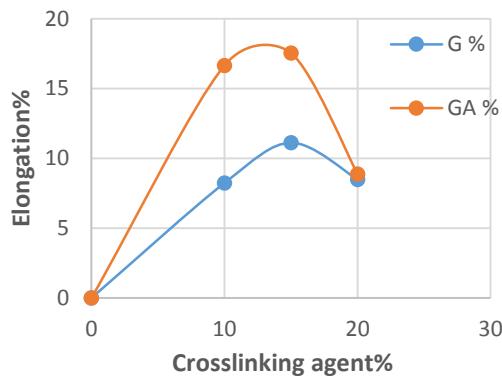


Figure 4: Elongation % of polymer blends A-F.

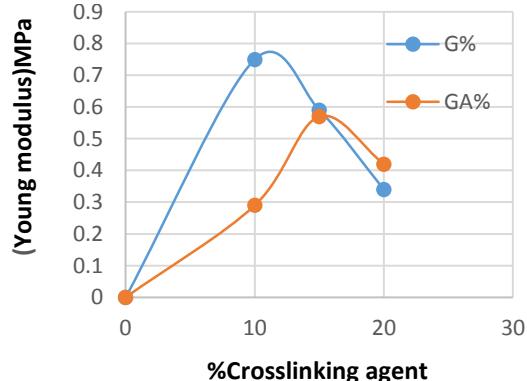


Figure 5: Elongation % of polymer blends A-F.

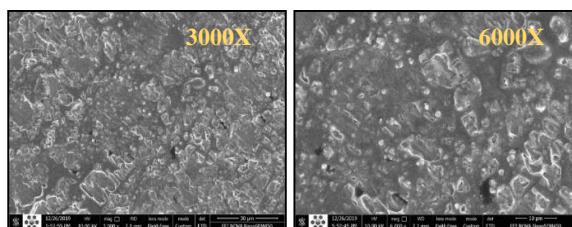


Figure 6: FESEM images of the B polymer blend with 3000X and 6000X amplifiers

Table 2: Mechanical properties parameters for polymer blends A-F.

Samples	σ_Y^b MPa	σ_M^c MPa	σ_B^d MPa	Young's Modulus (E) (MPa)	ϵ_M^e %	ϵ_B^f %
A	N/Aa	6.011	5.996	0.75	8.237	8.258
B	6.5773	6.577	4.777	0.59	11.115	12.884
C	2.861	2.861	0.569	0.34	8.480	17.903
D	4.851	4.851	4.267	0.29	16.651	18.528
E	9.881	9.881	1.957	0.57	17.533	28.775
F	3.741	3.741	2.927	0.42	8.876	11.898

^a Not applicable, ^b σ_Y : yield strength, ^c σ_M : maximum strength, ^d σ_B : maximum strength, ^e ϵ_M : maximum elongation, and ^f ϵ_B : elongation at break.

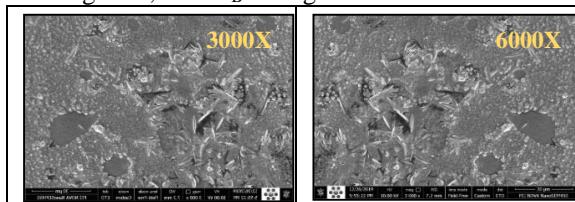
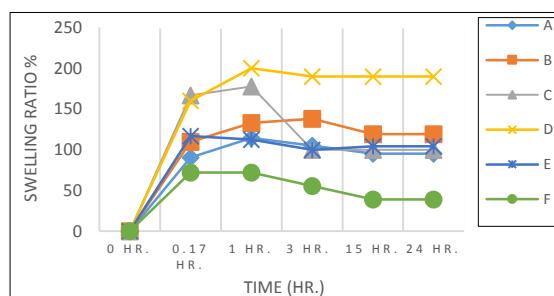


Figure 7: FESEM images of the E polymer blend with 3000X and 6000X amplifiers

4.3 Swelling study

The water absorption property of the hydrogels is represented in figure 8. It is depending on the crosslinking agent ratios in the polymer blends. All hydrogels reached equilibrium conditions at different times. The polymer blend **D** recorded the highest absorption rate of approximately 190%, and all the prepared polymer blends had a good ability to absorb water.

In any polymer network, the presence of ionic and hydrogen bonds in addition to high degree of crosslinking will enhance the water absorption in good quantities. As a result, the polymer will swell. The synthesized polymer blends showed very good swelling properties which enable them to be used as additives in water tanks. Especially in the desserts where the water so valuable and the current water tanks lose the water frequently during the storage.



5. Conclusion

Two crosslinking agents (Glutaraldehyde and Glyoxal) were used in three different ratios (10, 15, and 20%) to prepare several hydrogel blends along with an equal ratio of PVP/CMC/PVA. In addition to sorbitol as a plasticizer. The polymer blends with glyoxal as crosslinking agent showed the highest entanglement in the following order: **B>C>A>**. The highest elongation for hydrogel **B** was within the limits of 11.12%. While the polymer blends with glutaraldehyde as the entanglement agent were recorded in the following order: **E>D>F**. The polymer blend **E** scored the highest elongation at 17.53%. The prepared polymer blends recorded a significant rate of water absorption. The compound **D** recorded the highest absorption rate of approximately 190%, and all the prepared polymer blends had a good ability to absorb water during the first three hours. The polymer blends had maintained the water level in them for 24 hours. These polymer blends might be perfect candidates as wound dressing materials because their premium swelling property. They are flexible, semi-transparent, give tranquil feelings, easy to take off, and allowance the surveillance of the healing process. Furthermore, they seem very favorable for commercialization because of the cheapness and plenty of the substances and unpretentious low-cost methodology.

6. Conflicts of interest

There are no conflicts to declare

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