Poly (vinyl alcohol) - Chitosan Blends: Preparation, Mechanical and Physical Properties

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ABSTRACT

Poly (vinyl alcohol)-chitosan blend films were prepared by casting the respective polymer solutions. The glutaraldehyde was used as a cross-linking agent. A series of PVA-chitosan blends were prepared by varying the ratio of the constituents. Mechanical and physical properties of blended films such as tensile properties in the dry and wet states, water uptake, surface tension and contact angle were characterized. Blending PVA and chitosan improved strength and flexibility of the films in the dry and wet states. Cross-linking with glutaraldehyde improves tensile strength and decreases elongation of the films. PVA Content in the blends increases water uptake while cross-linking the films with glutaraldehyde causes less hydrophilicity. Water uptake in PVA-chitosan blends can be controlled by variation of their contents, cross-linking agent and the pH of solution. Blending of PVA and chitosan improves bulk and surface hydrophilicity of blended films.

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Key Words:
PVA;
chitosan;
blend; film;
preparation;
properties.

INTRODUCTION

Poly (vinyl alcohol), PVA, is a non-toxic, water-soluble synthetic polymer and has good physical and chemical properties and film-forming ability. The use of this polymer is important in many applications such as controlled drug delivery systems, membrane preparation, recycling of polymers and packaging. Studies on the mechanism of dissolution and changes in crystallinity and swelling behaviour of PVA and its physical gel-forming capabilities, have been carried out [1,2]. PVA Has bioinert-

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ness and it has many uses in medical applications such as artificial pancreas, hemodialysis, nanofilteration, synthetic vitreous and implantable medical device.
Anti-thrombogenicity, cell compatibility, blood compatibility and biocompatibility of PVA have been studied extensively [3-5].

Chitosan (Cs) is a natural polysaccharide formed during the deacetylation of chitin in alkaline condition. It comprises an unbranched chain consisting of β-(1→4) -2-amino-2-deoxy-D-glucopyranose, and it is a unique basic linear polysaccharide [6,9].

The hydrophilicity of the polymer due to amine functionality in most repeat units makes the polymer soluble in dilute acid [10]. Chitosan is widely used in food and pharmaceutical industry and in biotechnology. This polysaccharide has been extensively studied in the field of biomaterials and because of its biological properties, biodegradability, bioactivity and biocompatibility it has attracted much attention [11-16].

Polymer blending is one of the useful ways to have new material with required properties and there have been great scientific and commercial progress in the area of polymer blends. This was driven by the realization that new molecules are not always required to meet the need for new materials and blending can usually be implemented more rapidly and economically than the development of new materials [17,18].

Blends of synthetic and natural polymers represent a new class of materials and have attracted much attention especially in bioapplication as biomaterial. The success of synthetic polymers as biomaterial relies mainly on their wide range of mechanical properties, transformation processes that allow a variety of different shapes to be easily obtained and low production costs [17]. Biological polymers represent good biocompatibility but their mechanical properties are often poor, the necessity of preserving biological properties complicates their processability and their production costs are very high [19,20]. It is favourable that intermolecular interaction exists between two polymer species. Hydrophilicity of the synthetic polymers has great influence on the blend preparation and properties. Surface and bulk hydrophilicity of blended polymers affect mainly their biological behaviour. Bulk hydrophilicity of polymers may be studied by water uptake ratio, and surface hydrophilicity could be measured by surface tension and water contact angle. The PVA is a hydrophilic and water-soluble polymer and chitosan contains hydroxyl and amine groups. Some aspects, of their blend properties have been studied [21-26].

In this study, blended films were prepared from PVA and Cs with varying concentrations. The mechanical properties of these films were investigated by tensile strength and tensile strain of the blended films in the dry and wet states. As the bulk and surface hydrophilicity of biomaterials are very important parameters for bioapplication, we studied the effect of blending condition (such as component content, cross-linking and pH) on water uptake, contact angle and surface tension of different blended samples .

Materials

PVA Sample was purchased from Aldrich Co. (with 99% hydrolyzed, $\overline{M}_W$ 85,000-146,000). A sample of chitosan (Cs) was from Primex Co. (TM366), with 85.6% degree of deacetylation and viscosity of 115 cps in 1% acetic acid. All other chemicals used were analytical grade.

Methods

The polymer films were prepared by casting method. Cs Solutions were prepared by dissolving chitosan in 1% aqueous acetic acid solution at room temperature with stirring. The PVA was dissolved in hot water to form 10 %wt polymer solution. Both polymer solutions were filtered using sintered glass and the solutions were carefully mixed at various ratios. The weight fraction of PVA was different to obtain a series of blends with 0 to 100 %wt PVA in the resulting solution as listed in Table 1.

The filtered solution was placed under vacuum and

Table 1. The ratio of poly (vinyl alcohol) (PVA), chitosan (Cs) and the amount of glutaraldehyde (GA) in different samples.

Sample	Cs (%wt)	PVA (%wt)	GA x 10^{-5} (mol/g polymer)
S_1	100	0	0
$S_1(GA_1)$	100	0	2.4
S_2	75	25	0
$S_2(GA_1)$	75	25	2.4
S_3	50	50	0
$S_3(GA_1)$	50	50	2.4
$S_3(GA_2)$	50	50	5
$S_3(GA_3)$	50	50	7.5
S_4	25	75	0
$S_4(GA_1)$	25	75	2.4
S_5	0	100	0
$S_5(GA_1)$	0	100	2.4

Table 2. Properties of liquid used for contact angle and surface tension measurements.

Liquid	Surface tension (mN/m)	Polarity (mN/m)	Disperse (mN/m)
Water	72.8	46.8	26.0
Formamide	58.2	18.7	39.5
Diiodomethane	50.8	2.3	48.5

it was cast on a clean glass plate. Samples were dried at 60 C, immersed in NaOH (1N) and saturated Na_2SO_4 to remove residual materials then washed with deionized water to remove alkali and unreacted materials and finally dried at 60 C for 24 h. For cross-linking of the films a specific amount of glutaraldehyde was added to the solution, mixed thoroughly and it was cast as above.

EXPERIMENTAL

Tensile Properties

All the samples were prepared as thin films and their tensile strength and tensile strain in the dry and wet states were carried out using an Instron (model 5566, V=5 mm/min and d=10 mm). For testing in wet state, all the films were placed in phosphate buffer saline (PBS) solution (pH = 7.2 -7.4) for 30 min and then their tensile strength and tensile strain were measured.

Film strips in specific dimensions and free from air and bubble or physical imperfection were held between two clamps positioned at a distance 10 mm. During measurement, the sample was pulled by top clamp at a rate 5 mm/min.

The thickness of the film sample was measured using a micrometer at five locations (center and four corners), and the mean thickness was calculated. Samples with air bubbles, nicks or tears and having mean thickness variation of greater than 5% were excluded from analysis.

Water Uptake

The water uptake of different samples was calculated using the following method:

$$\text{Water uptake (\%)} = 100 \times (W_2 - W_1)/ W_1$$

Where, W_1 is the weight of completely dried sample and W_2 is the weight of swelled sample in the different pH buffer solution at 37 C for 1.0 h.

Surface Tension and Contact Angle

The contact angle of different liquids (listed in Table 2) on the surface of films with Sissil drop method were carried out using contact angle measurement system (model, Kruess-G10). All the measurements have been carried out at the same time (1 min). Each value was the mean of 7 measurements and reported with standard deviation. Water contact angle of films were meas-

Table 3. Tensile strength and tensile strain-at-break for different samples.

Sample	Tensile -(dry)		Tensile-(wet)	
	Strength (MPa)	Strain(%)	Strength (MPa)	Strain (%)
S_1	57.2 ± 1.6	9.0 ± 1.0	15.8 ± 1.1	40.9 ± 2.5
$S_1(GA_1)$	71.4 ± 1.3	7.5 ± 0.8	21.6 ± 1.6	31.7 ± 3.6
S_2	76.2 ± 2.1	10.0 ± 0.8	23.4 ± 1.7	48.1 ± 2.9
$S_2(GA_1)$	91.2 ± 1.9	8.9 ± 1.2	31.5 ± 1.3	39.2 ± 3.1
S_3	71.6 ± 1.5	11.2 ± 1.4	19.0 ± 1.8	55.6 ± 3.7
$S_3(GA_1)$	83.9 ± 2.3	10.0 ± 1.2	24.1 ± 1.4	46.5 ± 4.1
$S_3(GA_2)$	95.3 ± 2.0	8.2 ± 0.9	-	-
$S_3(GA_3)$	113.7 ± 1.2	4.1 ± 1.1	-	-
S_4	67.1 ± 1.1	14.8 ± 1.6	16.1 ± 1.3	68.0 ± 3.1
$S_4(GA_1)$	76.7 ± 1.4	13.3 ± 1.1	19.3 ± 1.5	62.2 ± 2.9
S_5	53.3 ± 1.9	16.2 ± 1.1	8.0 ± 1.5	80.1 ± 2.5
$S_5(GA_1)$	58.1 ± 2.5	15.4 ± 0.9	9.2 ± 1.0	76.1 ± 1.9

Table 4. Water uptake (pH =7, 1 h, 37°C) for different samples.

Sample	Water uptake (U %)
S_1	225 ± 20
$S_1(GA_1)$	155 ± 18
S_2	261 ± 31
$S_2(GA_1)$	187 ± 21
S_3	295 ± 17
$S_3(GA_1)$	230 ± 25
$S_3(GA_2)$	189 ± 16
$S_3(GA_3)$	140 ± 13
S_4	329 ± 14
$S_4(GA_1)$	251 ± 22
S_5	359 ± 18
$S_5(GA_1)$	309 ± 15

ured in the dry state and wet state (dipping the films in PBS solution in 37 C for 1.0 h and removing surface water with filter paper). Surface tension, polar and disperse part, were calculated by Owens method [26] .

Statistical Analysis

The results obtained from the mechanical and physical properties, were analyzed statistically using Microcal origin 1.3 software. Each result was the mean value of measurements and reported with standard deviation (mean values – SE).

RESULTS AND DISCUSSION

Tensile Properties

The tensile testing provides an indication of the strength and elasticity of the films, which can be reflected by strength and strain-at-break. The tensile strength and strain- at-break of different samples in dry and wet states were measured with Instron (Table 3). Blending ($p<0.05$) improved tensile strength of PVA-Cs blend in dry and wet states significantly. These results indicate that blend films have higher tensile strength than pure Cs and PVA films. Blending leads to an intermolecular interaction between two polymers and this improves mechanical strength of the blends. Kim and other research workers [21,22] have also supported these results. Due to possibility of interaction between -OH and $-NH_2$ groups in these two polymers, blending improves mechanical properties of the films. As it can be seen in Table 3, the tensile strength of S_1 sample is 57.2 MPa which increases to 76.2 MPa for S_2 sample (with 25 %wt PVA) and for S_3 sample (with 50 %wt PVA) increases to 71.6 MPa. PVA Sample has more elongation-at-break, so with increasing the PVA content in the blend, the flexibility of the films were increased.

Cross-linking with glutaraldehyde improves tensile strength and decreases tensile strain of the blend films. By increasing glutaraldehyde concentration, the films become more rigid and show less flexibility. It was found that the cross-linking improves mechanical properties of Cs as compared to PVA. The effect of glutaraldehyde to improve tensile strength increases by increasing Cs content in the blend films. The cross-linking of S_2 sample (25 %wt PVA) increased tensile strength by 20% in dry state and 36% in wet state. This percentages for S_4 samples (75 %wt PVA), in the dry and wet states were 13% and 20%, respectively. Similar trend was observed in the wet state. The cross-linking of chitosan and PVA with glutaraldehyde is shown in Figure 1.

Table 5. Surface tension (γ), polar part (γ_p) and contact angle (θ°) for different blend samples.

Sample	Contact angle(θ°)			Surface tension (mN/m)	
	Water	Formamide	Diiodomethane	(γ)	(γ_p)
$S_1(GA_1)$	58.2 ± 1.8	45.8 ± 1.7	38.9 ± 1.2	45.8	14.7
$S_2(GA_1)$	54.1 ± 2.3	43.5 ± 1.6	37.9 ± 1.5	47.6	17.1
$S_3(GA_1)$	53.2 ± 1.9	43.2 ± 2.0	37.3 ± 1.3	48.1	17.5
$S_4(GA_1)$	49.6 ± 2.5	41.8 ± 2.1	37.4 ± 1.0	49.5	20.2
$S_5(GA_1)$	45.8 ± 1.5	39.8 ± 1.8	36.5 ± 1.1	51.3	22.2

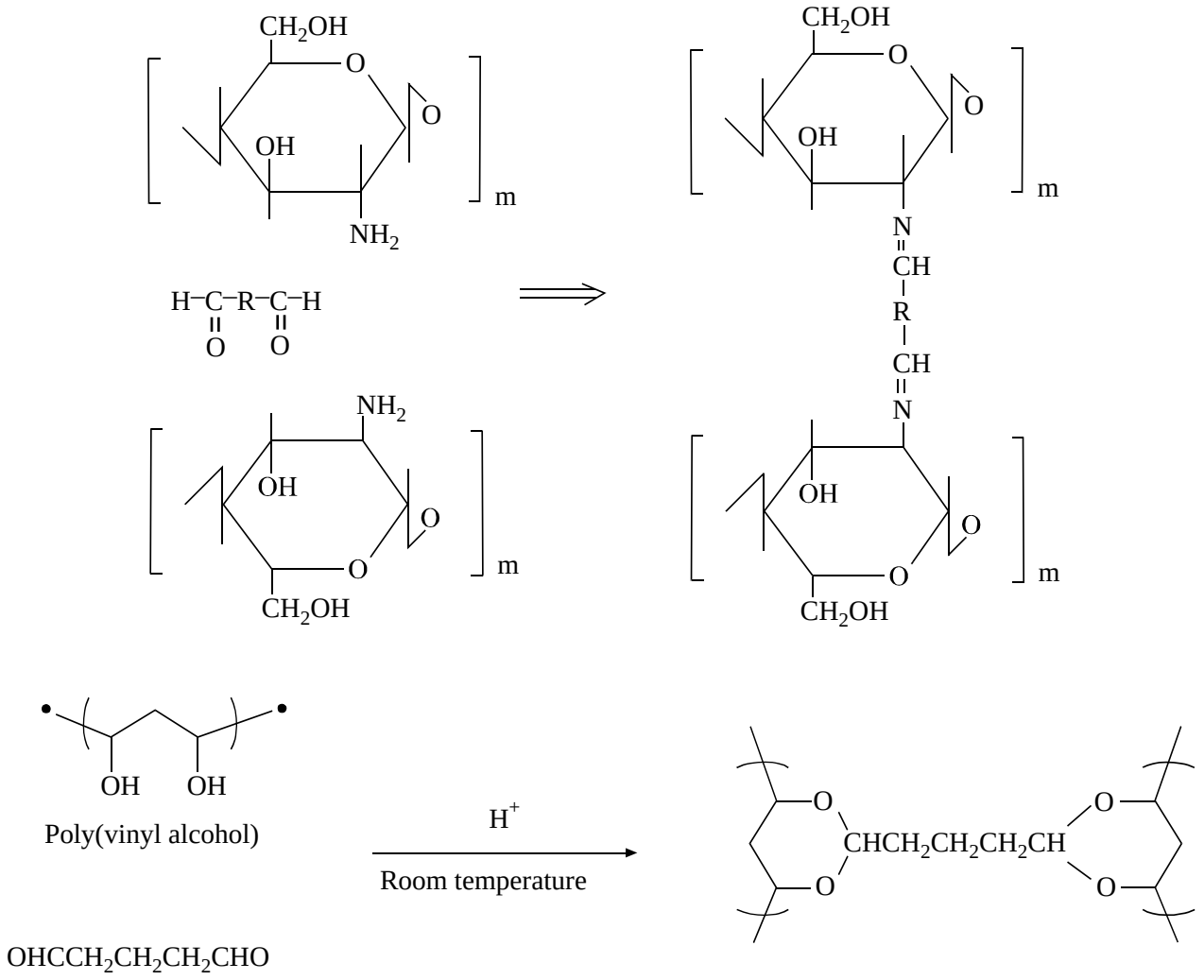
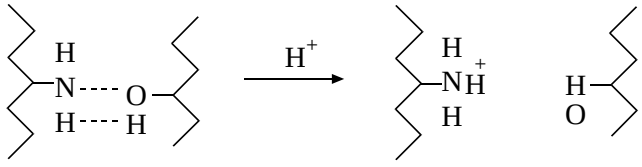


Figure 1. Schematic representation for cross-linking reaction of chitosan with GA [23] and cross-linking reaction of PVA with GA in acidic condition [3].

Water Uptake

As shown in Table 4 water uptake of all samples were increased by increasing the PVA content. This is attributed to the increasing of hydrophilic groups (-OH) in the blends. Cross-linking with GA decreases water uptake in all samples. By increasing GA concentration more hydroxyl and amino groups of polymers in the blends are consumed due to the cross-linking reactions and blends showing less capability for hydrogen bonding. The effect of pH on water uptake was also studied. The water uptake increased when pH decreased. The effect of pH on increasing water uptake is more significant for samples with more Cs content (Figure 2). The effect of pH on water uptake was decreased by increasing GA concentration (Figure 3). This could be explained by the fact that in acidic medium the amino groups of Cs ($-NH_2$) are protonized ($-NH_3^+$) so that the hydrogen bonds between Cs and PVA are inhibited, therefore, the network has more potential for hydrogen bonding with surrounding water. Also, Cs molecules in the acidic condition are being uncoiled and form rods [21], which, might be another parameter to enhance hydrogen bonding with water. It seems likely that pH has more effect to increase water uptake for Cs in comparison with PVA.



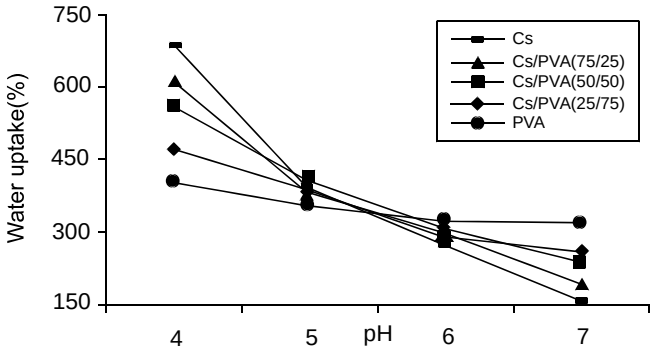


Figure 2. The effect of pH on water uptake for different cross-linked (GA_1 = 2.4 x 10^{-5} mol/g polymer) samples.

Surface Tension and Contact Angle

Surface and bulk hydrophilicity of materials influence their biological behaviour. Bulk hydrophilicity of polymers may be studied by water uptake measurement and surface hydrophilicity could be measured by surface tension and water contact angle. Surface tension (γ) is a direct measurement of intermolecular force at the surface. According to Fowkes theory, surface tension (γ) is separated in two main London dispersion forces (γ_d) and polar forces (γ_p) [27]. Contact angle measurement is an indirect empirical and semi-empirical method for determining surface energy and tension. The contact angle measurements have been used extensively to study surface homogeneity, changes in surface composition, hydrophilicity and hydrophobicity, migration of functional groups and low-energy component to the surface [28]. The increase in the polar component has been used as an indicator for migration of polar groups and could change (γ_d) and (γ_p). Some factors such as crystallinity and cross-linking influence the polymer

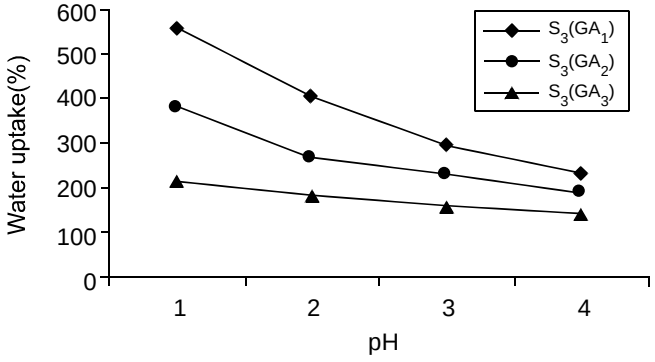


Figure 3. The effect of glutaraldehyde concentration (GA_1=2.4, GA_2=5, GA_3=7.5) x 10^{-5} mol/g polymer) and pH on water uptake for S3 (Cs/PVA-50/50) sample.

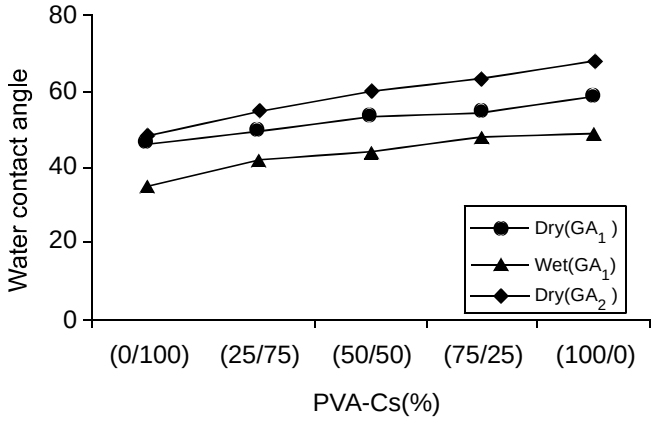


Figure 4. The effect of glutaraldehyde concentration (GA) on water contact angle (θ) for different samples in the dry and wet states.

mobility and migration of functional groups from surface into bulk or vice versa [29].

PVA Film (S_5) showed highest surface tension (Table 5) and with its increases in the blends, raised surface tension (γ) and polar part (γ_p). To evaluate the homogeneity and possibly phase separation of the films blend, water contact angle (θ) was measured both in the dry and wet states. Water contact angle (θ) for all samples in the wet state were lower than dry state. The effect of cross-linking with GA on hydrophilicity was decreased with increasing Cs content in the blend films (Figure 4). The water contact angles for both sides of the blends in wet state was almost the same as in the dry state; the difference observed was around 4-5 .

This is attributed to the probability of the polymer chains mobility, toward neighbouring molecules. The directions of hydrophilic groups in both sides in the dry state are different, therefore, the water contact angle for both surfaces are not the same. But in the wet state, both surfaces of blends are neighbouring with water molecules, and there is no difference between the water contact angle of either both side. In other words polar groups have shown mobility, from bulk to the surface. In the dry state the outer layer is air which is hydrophobic, so the hydrophilic groups could migrate to the inner bulk part. In the wet state the polar groups migrate towards the surface layer which is neighbouring with hydrophilic environment (water), therefore, water contact angle in dry state is greater than wet state.

The difference in water contact angle for both surfaces of blend films might be due to the segmental and functional mobility and migration of polymer chains in the blend, and not due to phase separation of blended

components.

As shown in Figure 4 in cross-linking with GA, the polar groups like (-OH) and (-NH_2) participate in cross-linking reaction so their mobility to the surface was decreased and the water contact angle in the dry and wet state has been increased.

CONCLUSION

In this study the blending of PVA and chitosan (Cs) improves tensile strength and flexibility of blended films both in dry and wet states. Cross-linking with glutaraldehyde improves tensile strength and decreases elongation of blends. Cross-linking effect of glutaraldehyde increases by increasing the Cs content. As the bulk and surface hydrophilicity of biomaterials are very important parameter for bioapplication, we studied the effect of component content, cross-linking and pH on water uptake, contact angle and surface tension of different blended samples. With increasing PVA content in the blends, water uptake increases. Cross-linking of the blends with glutaraldehyde decreases water uptake. The water uptake increases when pH decreased. The effect of pH on increasing water uptake, is more significant for samples with more Cs content and the effect of pH on water uptake decreases when glutaraldehyde concentration is raised. It seems likely that pH has more effect to increase water uptake for Cs in comparison with PVA. Water uptake in PVA-chitosan blend films can be controlled by variation of their contents, cross-linking agent and the pH of solution. PVA Films showed highest surface tension and with its increases in the blends, surface tension (γ) and polar part (γ_p), were increased. Cross-linking with glutaraldehyde increases water contact angle. It seems likely that, the blended films are homogeneous on both sides. Blending the PVA with Cs improves tensile strength, flexibility, bulk and surface hydrophilicity of the blended films.

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