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## Mechanical Reinforcement of Wool Fiber through Polyelectrolyte Complexation with Chitosan and Gellan Gum

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**Abstract:** The formation of polyelectrolyte complex (PEC) wool fibers formed by dipping chitosan or gellan gum-treated wool fibers into biopolymer solutions of opposite charge is reported. Treating wool fibers with chitosan (CH) and gellan gum (GG) solutions containing food dyes resulted in improved mechanical characteristics compared to wool fibers. In contrast, pH modification of the solutions resulted in the opposite effect. The mechanical characteristics of PEC-treated fibers were affected by the order of addition, *i.e.*, dipping GG-treated fibers into chitosan resulted in mechanical reinforcement, whereas the reverse-order process did not.

**Keywords:** mechanical properties; polyelectrolyte complex; chitosan; gellan gum; wool

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### 1. Introduction

Polyelectrolyte complexes (PECs) have attracted the interest of scientists not only to solve the mechanism of polyelectrolyte complexation [1,2], but also to develop a wide range of applications, such as nanofiltration [3], coating [4], tissue engineering [5,6] and encapsulation [7]. Polyelectrolyte

complexes have been successfully developed on a number of different substrates including glass, quartz, mica, silicone, gold and silver [8].

To date, only a few papers have described the coating and dyeing of textile fabrics using the polyelectrolyte complexation technique. For example, Polowinski's team has used this technique to modify the surface of textile fabrics to acidic or basic and then treated with the opposite charges [9–11]. This process changes the surface charge, hydrophilicity and electro-kinetic potential, as well as improving dye absorbing capability. Dubas *et al.* also successfully coated nylon and silk fibers containing silver nanoparticles using a polyelectrolyte complex [12]. The resulting fibers exhibited antimicrobial activity against *Staphylococcus aureus* of up to 80%.

Natural polysaccharides such as chitosan (CH) and gellan gum (GG) are suitable materials for polyelectrolyte complexation. Chitosan is a linear cationic polyelectrolyte derived from chitin, one of the most abundant polysaccharides occurring in nature [13]. Gellan gum is a linear anionic polysaccharide produced by *Sphingomonas elodea* bacteria [14]. Chitosan and gellan gum are attractive polyelectrolytes due to their biocompatibility and biodegradability. For example, GG is approved by the US Food and Drug Administration (FDA) and the European Union (E 415) for use in the food industry and is an emerging scaffold material for tissue engineering applications [15]. To date, a limited number of CH-GG polyelectrolyte complexes have been reported which focus on the development of capsules and fibers [16–20]. Our recent work has shown that free-standing films can be formed using polyelectrolyte complexation of CH and GG [21] and that these dual-layer films can be engineered to exhibit antibacterial activity while supporting growth of cells [22].

In this paper, we describe the formation of polyelectrolyte complexes of chitosan and gellan gum using wool fibers as a substrate material. Pristine wool fibers were first coated with either chitosan or gellan gum to modify the fiber surface. These so-called “single-treated” wool fibers were then immersed in solutions of opposite charge to form PEC-treated wool fibers. The effects of immersion duration, dyeing, pH adjustment and order of addition of single-treated and PEC-treated wool fibers on the mechanical properties are discussed.

## 2. Experimental Section

### 2.1. Materials

Chitosan (CH; medium molecular weight,  $M_w \approx 1.9\text{--}3.1 \times 10^5$  g/mol, 75% degree of deacetylation (DD), viscosity  $\approx 453$  mPa s (1% (w/v) chitosan in 1% acetic acid), product number 448877–lot number 07918TE), and glycerin were obtained from Sigma Aldrich, Australia. Gellan gum (GG; low acyl,  $M_w \approx 2\text{--}3 \times 10^5$  Da, lot number 7K 1383A) was a gift from CP Kelco, USA. According to the manufacturer's specification, all acyl groups have been removed from the glucose residue for this form of gellan gum. Pristine wool fiber (100% wool, in strand of 4 thinner wools, dreamtime, colour 0051 (light colour), lot number 760840) were purchased from Patons, Australia. Food dyes (blue and yellow) were purchased from Queen Essence Food Colours, Australia. All materials were used as received.

## 2.2. Preparation of Chitosan and Gellan Gum Solutions

CH (2% (w/v)) and glycerine (0.6% (w/v)) were dissolved in an acetic acid (0.08 M) solution under continuous stirring for 2 h at 70 °C. GG (1% (w/v)) and glycerine (0.5% (w/v)) were dissolved in Milli-Q water (resistivity, 18.2 MΩ cm) under continuous stirring for 2 h at 70 °C. The pH values of these as-prepared CH and GG solutions were pH ~5.6 and pH ~5.4, respectively. CH and GG solutions with pH ~1.8 (CH) and pH ~12 (GG) were prepared from the as-prepared solutions through addition of concentrated acetic acid (glacial, 17 M) and sodium hydroxide (1 M), respectively. CH-dyed and GG-dyed solutions were prepared by additions of 0.25% (v/v) of blue and yellow food dyes, respectively.

## 2.3. Single Treated Fiber

CH treated fiber (CH-fiber) and GG treated fiber (GG-fiber) were prepared by immersing pristine wool fibers into CH solution (25 °C) and GG solution (70 °C) in a beaker for 2, 5, 10, 20 and 30 min. CH-dyed and GG-dyed fibers were prepared by immersing wool fibers into CH-dyed and GG-dyed solutions for 20 min and 5 min, respectively.

## 2.4. Polyelectrolyte Complex Treated Wool Fiber

Polyelectrolyte complex (PEC) wool fibers were prepared by immersing CH-dyed and GG-dyed fibers into solutions of opposite charge (*i.e.*, GG-dyed solution or CH-dyed solution) for 20 min and 5 min, respectively. The CH-dyed fiber immersed into the GG-dyed solution is hereafter referred to as CH<sup>int</sup> °GG, whereas GG-dyed fiber immersed into the CH-dyed solution is hereafter referred to as GG<sup>int</sup> °CH. The pH adjusted of dyed-fibers or dyed solutions indicated by the addition of “pH” to the name. For example, a PEC fiber prepared by immersing a pH adjusted CH-dyed fiber into GG-dyed solution is hereafter referred to as CH(pH)<sup>int</sup> °GG.

## 2.5. Drying the Treated Fiber

Single treated fiber and polyelectrolyte complex treated fiber were dried under controlled ambient conditions (21 ± 0.5 °C, 60 ± 10% relative humidity) for 2 days using a temperature humidity chamber (Thermoline Scientific), and pre-conditioned for another 2 days under the same controlled ambient conditions (21 ± 0.5 °C, 60 ± 10% relative humidity) prior to testing.

## 2.6. Characterization

Stress-strain measurements were obtained using an Instron Universal Testing Machine model 5565 with ± 10 kN grips and cross-head speed 20 mm/min. The treated fibers were cut to 100 mm and the diameters (containing 4 strands of twisted thinner wool) were measured with an optical microscope (Leica Z16 APO) and analyzed with Leica Application Suite (version 3.1.0 R1). Young's modulus (E), tensile strength (TS), and work of extension (U) were calculated from the slope of the linear part of the stress/strain curve, the maximum stress, and by integrating the area under the stress/strain curve, respectively. Extension or elongation (ε) was also recorded.

The pH of solutions and treated-wool fibers were measured using a Metrohm 826 pH mobile pH meters. The cross-section of treated wool fibers were imaged using the optical microscope.

### 2.7. Kubelka-Munk Analysis

The images of dyed-wool fiber were captured by the optical microscope and saved in 8-bit colour format (including red, green and blue channels). These images were analyzed using the Kubelka-Munk (K-M) equation (1) for each of the three channels,

$$[K/S = (1 - R)^2/2R] \quad (1)$$

where  $K$  is the coefficient of absorption,  $S$  is scattering spectrum, and  $R$  is the fraction of light reflected. The ratio ( $K/S$ ) obtained is proportional to the “concentration” of the colourant. A minimum of 5 measurements were made across the dyed-wool fiber to calculate the mean value.

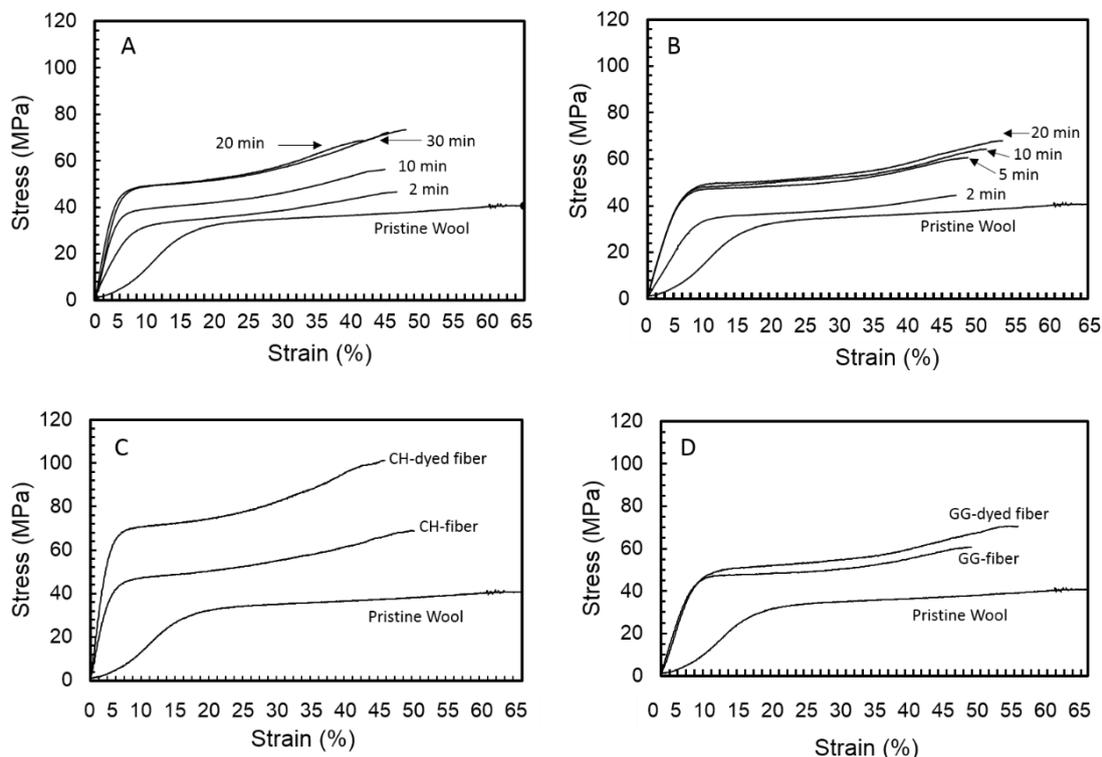
## 3. Results and Discussion

### 3.1. Single-Treated Fiber

The mechanical properties of pristine wool fibers immersed in CH (CH-fiber) and GG (GG-fiber) solutions at 25 °C and 70 °C, respectively are shown in Figure 1 and Table 1. Gellan gum solutions were kept at a temperature (~ 70 °C) above the gelation temperature (30 °C). The immersion time to reach mechanical reinforcement was shorter for GG (5 min) than for the CH solution (20 min), see Figure 1A,B and Table 1. The higher temperature for GG also affected the persistence length (chain stiffness) which has been previously reported as  $\leq 9.4$  nm at 40 °C [23]. In contrast, the corresponding value for CH is 81 nm at 25 °C [24]. In other words, it is assumed that GG chains are more flexible (less stiff) compared to CH chains and thus diffuse easily into wool fiber.

Treated CH-fiber and GG-fiber at 20 min and 5 min, respectively showed that the tensile strength (TS), Young's modulus (E) and work of extension (U) values increased significantly compared to the corresponding values for pristine wool fiber (Table 1). For example, the E of CH-fiber (20 min) and GG-fiber (5 min) increased by 5-fold and 4-fold, respectively. However, the treatment of wool fiber with CH and GG comes at a cost of reduce values for extension ( $\epsilon$ ). The loose structure of pristine wool fiber (consisting strand of 4 thinner wools) yielded  $\epsilon = 64 \pm 2\%$ . This reduced to  $50 \pm 3\%$  and  $54 \pm 1\%$  for the CH-fiber and GG-fiber, respectively.

**Figure 1.** (A,B) Stress-strain curves of single-treated fiber at different duration of immersions; (A) chitosan (CH)-fiber, (B) gellan gum (GG)-fiber, (C,D) the comparison of stress-strain of dyed and un-dyed fibers; (C) CH at 20 min of immersion and (D) GG at 5 min of immersion.



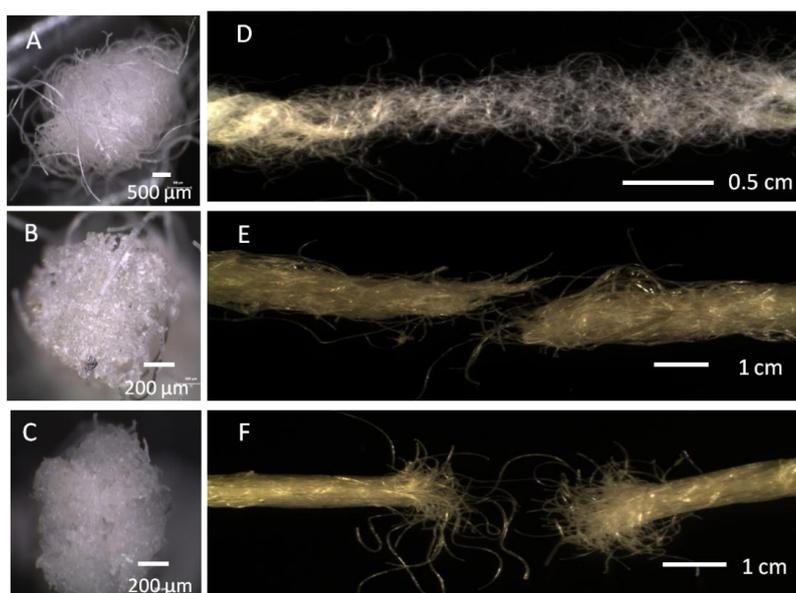
**Table 1.** Mechanical properties of CH-fiber and GG-fiber at different immersion duration times. Tensile strength (TS), Young’s modulus (E), work of extension (U) and extension ( $\epsilon$ ) for different single-treated fiber are given.

Sample	Immersion (min)	Diameter ( $\mu\text{m}$ )	TS (MPa)	E (MPa)	U ( $\text{J g}^{-1}$ )	$\epsilon$ (%)
Pristine wool fiber	-	850 $\pm$ 30	41 $\pm$ 1	270 $\pm$ 24	19 $\pm$ 11	64 $\pm$ 2
CH-fiber	2	930 $\pm$ 10	49 $\pm$ 4	662 $\pm$ 52	31 $\pm$ 8	47 $\pm$ 2
	10	880 $\pm$ 40	55 $\pm$ 5	1103 $\pm$ 117	30 $\pm$ 3	48 $\pm$ 2
	20	800 $\pm$ 30	65 $\pm$ 4	1447 $\pm$ 191	33 $\pm$ 1	50 $\pm$ 3
	30	760 $\pm$ 40	73 $\pm$ 7	1400 $\pm$ 250	27 $\pm$ 8	49 $\pm$ 6
GG-fiber	2	870 $\pm$ 70	48 $\pm$ 8	567 $\pm$ 181	32 $\pm$ 2	50 $\pm$ 1
	5	800 $\pm$ 70	61 $\pm$ 9	1001 $\pm$ 155	38 $\pm$ 1	54 $\pm$ 1
	10	780 $\pm$ 50	61 $\pm$ 7	932 $\pm$ 143	34 $\pm$ 4	54 $\pm$ 1
	20	770 $\pm$ 20	69 $\pm$ 7	1004 $\pm$ 56	36 $\pm$ 7	54 $\pm$ 1

The mechanism of mechanical reinforcement of CH-fiber and GG-fiber is likely to be the results of interactions between functional groups present in wool fiber, CH and GG. It has been shown that pristine wool fiber contains hydroxyl, amino, imino and sulphhydryl functional groups [25,26]. Chitosan and gellan gum have hydroxyl and amine and carboxylic functional groups, respectively. It is suggested that the functional groups of wool fiber interact with the amine and hydroxyl groups of

chitosan, and with the hydroxyl and carboxyl groups of gellan gum [27]. Figure 1 and Table 1 show that the reinforcement CH-fiber (20 min immersion,  $E = 1447 \pm 191$  MPa) is larger than GG-fiber (5 min immersion,  $E = 1001 \pm 155$  MPa). The reinforcement with chitosan has previously been linked to the van der Waals interaction [28,29]. Optical analysis of the cross-section and fracture topography for the fibers supports the difference in reinforcement (Figure 2).

**Figure 2.** (A–C) Cross sectional area of single-treated fibers; (A) pristine wool fiber, (B) CH-fiber after 20 min of immersion; (C) GG-fiber after 5 min of immersion; (D–F) fractured topography (side view) of treated fibers from tensile testing; (D) pristine wool fiber; (E) CH-fiber after 20 min of immersion and (F) GG-fiber after 5 min of immersion.



CH-fiber shows a strong inter-fiber bonding (Figure 2B) as well as a clean fracture topography (Figure 2E). In contrast, the fracture topography of GG-fibers suggests weaker bonding, based on the number of fiber strands pulled out from the GG matrix (Figure 2F). In what follows, CH-fiber (20 min) and GG-fiber (5 min) are used in the preparation of dyed-fiber, pH adjusted fiber and PEC-treated fibers.

### 3.2. Dyed Single-Treated Fiber

CH and GG solutions are typically optically transparent. To assist with the observation of polyelectrolyte complex formation, the GG and CH solutions were spiked with blue and yellow dyes, respectively. Hence, if PEC occurs then the fiber color should turn from blue (or yellow) to green. Treating CH-fiber in blue dye solution (hereafter referred to as CH-dyed fiber) shows a significant improvement for the TS and E values, see Figure 1C,D and Table 2. For example, the TS and E values of CH-dyed fibers improved by 62% and 64%, respectively than CH-fiber. The GG-dyed fibers exhibited a modest improvement in TS values of 18% compared to GG-fiber. However, the U values of CH-dyed and GG-dyed fibers decreased, whereas  $\epsilon$  does not significantly change compared to CH-fiber and GG-fiber (see also Table 2).

**Table 2.** Mechanical properties of dyed single-treated fiber (unless stated otherwise), pH adjusted single-treated fiber and dyed with pH adjusted polyelectrolyte complex (PEC)-treated fibers. CH-fibers and CH solutions were dyed with blue food color; and GG-fibers and GG solutions were dyed with yellow food color. Single-treated fibers immersed in CH and GG solution for 20 min and 5 min, respectively. For PEC-treated fibers, CH single-treated fiber immersed in GG solution for 20 min (CH<sup>int</sup> °GG) and GG single-treated fiber immersed in CH solution for 5 min (GG<sup>int</sup> °CH). Tensile strength (TS), Young's modulus (E), work of extension (U) and extension ( $\varepsilon$ ) of treated fibers are given.

Sample	Diameter ( $\mu\text{m}$ )	TS (MPa)	E (MPa)	U ( $\text{J g}^{-1}$ )	$\varepsilon$ (%)
Pristine wool fiber	850 $\pm$ 30	41 $\pm$ 1	270 $\pm$ 24	19 $\pm$ 11	64 $\pm$ 2
CH	800 $\pm$ 30	65 $\pm$ 4	1447 $\pm$ 191	33 $\pm$ 1	50 $\pm$ 3
GG	800 $\pm$ 70	61 $\pm$ 9	1001 $\pm$ 155	38 $\pm$ 1	54 $\pm$ 1
CH-dyed	620 $\pm$ 40	105 $\pm$ 9	2380 $\pm$ 275	28 $\pm$ 2	48 $\pm$ 2
GG-dyed	680 $\pm$ 50	72 $\pm$ 9	959 $\pm$ 103	31 $\pm$ 0.3	58 $\pm$ 2
CH(pH)	740 $\pm$ 60	82 $\pm$ 9	1577 $\pm$ 257	30 $\pm$ 1	52 $\pm$ 1
GG(pH)	660 $\pm$ 40	42 $\pm$ 4	814 $\pm$ 150	23 $\pm$ 2	63 $\pm$ 3
CH <sup>int</sup> °GG	620 $\pm$ 60	111 $\pm$ 14	2356 $\pm$ 108	26 $\pm$ 0.4	48 $\pm$ 2
GG <sup>int</sup> °CH	690 $\pm$ 50	92 $\pm$ 7	1290 $\pm$ 109	32 $\pm$ 0.6	58 $\pm$ 1
CH <sup>int</sup> °GG(pH)	730 $\pm$ 40	43 $\pm$ 3	1065 $\pm$ 111	17 $\pm$ 0.6	57 $\pm$ 2
GG <sup>int</sup> °CH(pH)	700 $\pm$ 60	69 $\pm$ 16	798 $\pm$ 140	36 $\pm$ 1.5	59 $\pm$ 2
CH(pH) <sup>int</sup> °GG	790 $\pm$ 70	64 $\pm$ 3	949 $\pm$ 83	34 $\pm$ 1	58 $\pm$ 2
GG(pH) <sup>int</sup> °CH	690 $\pm$ 30	63 $\pm$ 1	918 $\pm$ 66	28 $\pm$ 0.1	70 $\pm$ 5
CH(pH) <sup>int</sup> °GG(pH)	750 $\pm$ 60	36 $\pm$ 2	769 $\pm$ 60	20 $\pm$ 0.8	60 $\pm$ 2
GG(pH) <sup>int</sup> °CH(pH)	650 $\pm$ 30	60 $\pm$ 3	945 $\pm$ 155	26 $\pm$ 0.6	70 $\pm$ 1

The improved TS and E of CH-dyed and GG-dyed fibers could be attributed to the bonding of active ingredients of food dyes to the functional groups of CH and GG. The ingredients of blue and yellow food dyes as obtained from the manufacturer are concentrated dye (anthraquinone and triphenylmethane), citric acid, a synthetic colorant (E124, Ponceau for blue and E102, Tartrazine for yellow) and preservative (E211, sodium benzoate). Citric acid may form H-bonds with hydroxyl groups and amino groups of CH as well as enabling ester crosslinking [30,31]. Anthraquinone and triphenylmethane compounds are also expected to interact with hydroxyl groups and amino groups in CH [32], which is reflected in improved TS and E values of CH-dyed fiber. The GG-dyed fiber results showed that the TS improved, which may be a result of hydrogen bonding interactions between citric acid to carboxyl groups of GG [33].

### 3.3. pH Adjusted Single-Treated Fiber

Pristine wool fibers immersed in pH adjusted dyed solutions of CH (pH = 1.8) and GG (pH = 12), respectively showed that TS and E values decreased, while  $\varepsilon$  values increased (Table 2). For example, the TS value of CH-dyed (pH) fibers decreased to 82  $\pm$  9 MPa compared to the corresponding value of CH-dyed fiber (TS = 105  $\pm$  9 MPa, Table 2). The decrease in U and E values of the CH-dyed (pH) and GG-dyed (pH) fibers is likely related to a lower amount of functional groups available to interact with

functional groups of wool fibers [25]. It is well known that, CH solution will be protonated in acidic solution ( $\text{pH} = 1.8$ ), leading to a reduction in the amount of available amine groups. In contrast, GG will be deprotonated in basic solution ( $\text{pH} = 12$ ), *i.e.*, this reduces the amount of available carboxyl groups.

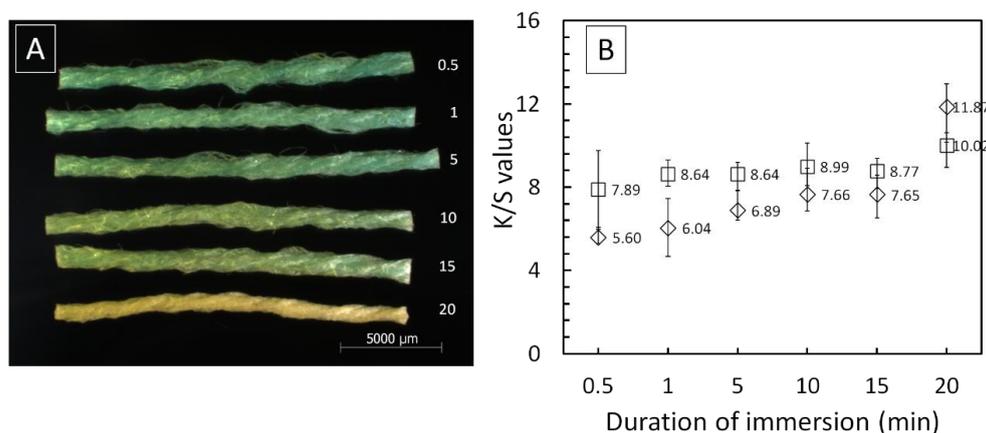
### 3.4. Dye and pH Adjusted Polyelectrolyte Complex Treated Fiber

The mechanical properties of dyed and pH adjusted polyelectrolyte complex (PEC)-treated fibers are summarized in Table 2.  $\text{CH}^{\text{int}} \text{GG}$  PEC-treated fibers exhibited an increase in TS values, but no significant change in E, U and  $\varepsilon$  values compared to single-treated CH-dyed fibers. Modification of the pH of  $\text{CH}^{\text{int}} \text{GG}$  PEC-treated fiber; *i.e.*, fiber and/or solution ( $\text{CH}^{\text{int}} \text{GG}(\text{pH})$ ,  $\text{CH}(\text{pH})^{\text{int}} \text{GG}$ , and  $\text{CH}(\text{pH})^{\text{int}} \text{GG}(\text{pH})$ ) did not result in mechanical reinforcement compared to single-treated CH-dyed and CH-dyed (pH) fibers. Nonetheless, these PEC-treated fibers (PEC, dyed, pH-modified) showed that the mechanical characteristics are comparable to single-treated GG-dyed or GG-dyed (pH) fibers (Table 2). For example, the TS, E, U and  $\varepsilon$  values of  $\text{CH}^{\text{int}} \text{GG}(\text{pH})$  PEC-treated fiber were  $43 \pm 3$  MPa,  $1065 \pm 111$  MPa,  $17 \pm 0.6 \text{ J g}^{-1}$  and  $57 \pm 2\%$ , respectively. Similar observations were made for the  $\text{CH}(\text{pH})^{\text{int}} \text{GG}$  and  $\text{CH}(\text{pH})^{\text{int}} \text{GG}(\text{pH})$  PEC-treated fibers (Table 2). These fibers exhibit mechanical characteristics comparable to those of single-treated GG-dyed and GG-dyed (pH) fibers, respectively. In contrast,  $\text{GG}^{\text{int}} \text{CH}$  PEC-treated fiber showed significant improvements in TS and E values compared to GG-dyed fiber (Table 2). pH modification of  $\text{GG}^{\text{int}} \text{CH}$  (fibers and solutions) resulted in mechanical reinforcement of  $\text{GG}^{\text{int}} \text{CH}(\text{pH})$ ,  $\text{GG}(\text{pH})^{\text{int}} \text{CH}$  and  $\text{GG}(\text{pH})^{\text{int}} \text{CH}(\text{pH})$  PEC-treated fibers compared to single-treated GG-dyed or GG-dyed (pH) fibers (Table 2).

Why do the mechanical characteristics of PEC-treated wool change by reversing the order of addition? There are a number of differences between CH and GG materials which are likely to play a role: (i) CH has an intrinsic  $\text{pK} = 6.5$  [34], while GG has an intrinsic  $\text{pK} = 3.5$  [35] over a wide range of solution pH; (ii) The pH of CH-dyed fiber are always near neutral, regardless of the pH of CH-dyed solution used to immerse the fibers. For example, CH-dyed solutions of  $\text{pH} = 1.76 \pm 0.04$  and  $\text{pH} = 5.54 \pm 0.04$  resulted in CH-dyed fibers with the pH values of  $6.8 \pm 0.05$  and  $7.3 \pm 0.05$ , respectively. GG-dyed solutions of  $\text{pH} = 5.57 \pm 0.04$  and  $12.15 \pm 0.12$  resulted in GG-dyed fibers with pH values of  $5.91 \pm 0.09$  and  $8.95 \pm 0.13$ , respectively; and (iii) chain stiffness or the persistence length of CH ( $\text{DD} = 93\%$ ) is 81 nm at  $25 \text{ }^\circ\text{C}$  [23], whereas GG is 9.4 nm at  $40 \text{ }^\circ\text{C}$  [24].

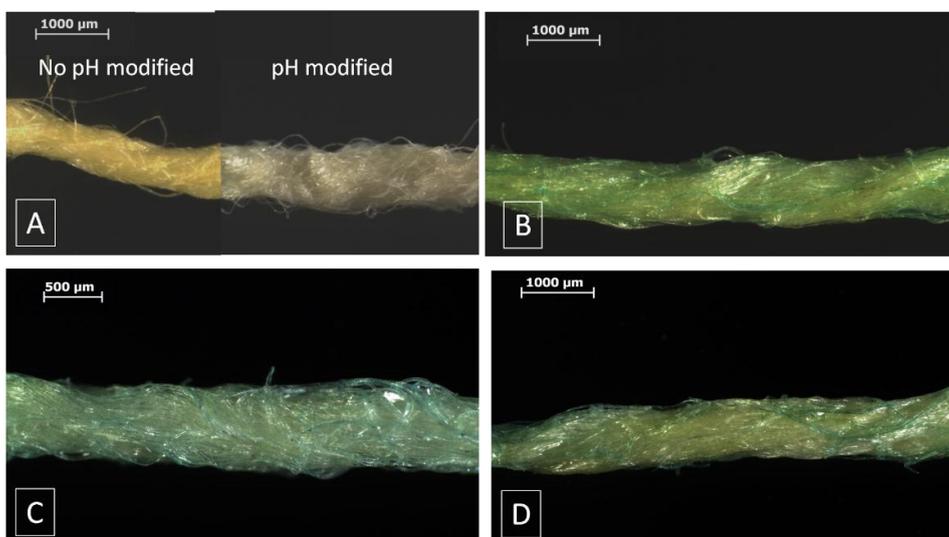
From the difference in pH of CH-dyed fiber and GG-dyed solution as well as persistence length of CH and GG, it is likely that the mechanical characteristics of  $\text{CH}^{\text{int}} \text{GG}(\text{pH})$ ,  $\text{CH}(\text{pH})^{\text{int}} \text{GG}$ , and  $\text{CH}(\text{pH})^{\text{int}} \text{GG}(\text{pH})$  PEC-treated fibers are governed by diffusion of GG into CH-dyed fiber. This argument is in agreement with the observed color changes shown in Figure 3A. Initially, CH-dyed (pH) and GG-dyed (pH) (both fibers and solutions) are blue and yellow, respectively. By dipping CH-dyed (pH) fibers into GG-dyed (pH) solution, the color of this PEC-treated fiber changed to green for 0.5, 1 and 5 min of immersion (Figure 3A).

**Figure 3.** (A) Color transformation of CH(pH)<sup>int</sup> GG(pH) PEC-coated fiber at 0.5, 1, 5, 10, 15 and 20 min of immersions and (B) K/S values of red (◇) and green (□) channels as a function of duration of immersions.



The green color partially changed to yellow after 10 min of immersion and completely changed to yellow after 20 min immersion. The change in color from green back to yellow may indicate the build-up of an outer GG layer on top of the PEC layer. These color changes were also followed using Kubelka-munk analysis [36]. In contrast, CH is unable to penetrate into GG in GG<sup>int</sup> CH, GG<sup>int</sup> CH(pH) and GG(pH)<sup>int</sup> CH(pH) PEC-treated fibers as shown in Figure 4.

**Figure 4.** (A) Single-coated fibers GG-dyed fibers before and after pH modification, (B-D) PEC-coated fibers; (B) GG<sup>int</sup> CH, (C) GG<sup>int</sup> CH(pH) and (D) GG(pH)<sup>int</sup> CH(pH). Those PEC-coated fibers are covered with a green colour on the outer layer and yellow colour at core of each fiber.



#### 4. Conclusions

PEC wool fibers were developed by polyelectrolyte complexation of chitosan and gellan gum. Pristine wool fibers treated with GG and CH displayed their optimum mechanical reinforcement after immersion of 5 min and 20 min, respectively. Incorporating a dye in the biopolymer solutions resulted

in improved mechanical properties compared to fibers prepared without dyes. In contrast, preparing fibers with pH modified dye solutions resulted in a decrease in the mechanical characteristics. PEC fibers were prepared by dipping biopolymer treated fibers into biopolymer solutions of opposite charge. The order of addition was found to affect the mechanical characteristics of the PEC fibers. It is suggested that the difference in observed mechanical characteristics is due to the ability of GG to diffuse into CH-dyed fiber, and the inability of CH to diffusion in GG-dyed fibers. This paper contributes to the development of biopolymer reinforced textile materials.

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### Conflicts of Interest

The authors declare no conflict of interest.

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